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SYNTHESIS AND CHARACTERIZATION OF COPOLY
(AMIDE-IMIDE-SULFONAMIDES)

by

Stephen C. Liptak

June, 1986

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

APPROVED:

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ABSTRACT

Commercially available aromatic diamines such as 4,4'-oxydianiline and 4,4'-methylenedianiline were treated with N-acetamidobenzenesulfonyl chloride to give the amino-sulfonamido-acetanilide derivatives. These derivatives were treated with 6M hydrochloric acid to give the diamine monomers containing a preformed sulfonamide linkage. These monomers were polymerized with various bisimide diacids using the Yamazaki reaction. Polymerizations involving a low temperature solution technique were also investigated.

The polymers obtained were characterized using infrared spectroscopy, thermal gravimetric analysis, differential scanning calorimetry, and dilute solution viscosity.

Inherent viscosities of the prepared polymers ranged from 0.08 to 0.54 dL/gm. In spite of low inherent viscosities, the polymers had film forming properties, with all but one being clear, flexible, and slightly colored.

Glass transition temperatures, determined by differential scanning calorimetry, ranged from 266 to 324°C. Thermogravimetric analyses of the polymers showed that they have moderate thermal stability with polymer decomposition temperatures ranging from 361 to 417°C and weight losses ranging from 4.13% to 11.28% at 360°C in nitrogen.

ACKNOWLEDGEMENTS

I wish to express my sincere thanks to my research advisor, Dr. Jerry Adduci, for his continuous guidance and support throughout this project. I also wish to thank my graduate committee, the Rochester Institute of Technology for the funding of this project and Sharon Casper for her help in the evaluation of the thermal properties of the prepared polymers.

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1.0 INTRODUCTION

The largest and most important group of linear-acyclic nitrogen containing polymers are the polyamides. The extensive research in this area is due to the success of the aliphatic and, later, the aromatic systems which have been developed into commercial products. Another contributing factor is undoubtedly the simplicity of the system and the many varied routes to amide functions. In essence, the only monomers necessary are diacids and diamines (or an amino acid), or derivative thereof. Polyamides can also be prepared by the ring opening polymerization of lactams.

Because of the commercial success of aliphatic polyamides, aromatic systems were a predictable extension of research by fiber producers such as E. I. du Pont de Nemours Co., and Monsanto Corp. Given this new drive and the desirable properties of the all aromatic polymers, this class of materials was one of the first to be exploited on a large scale as thermally stable polymers.

The search for thermally stable resins usable at 500°C for long periods of time has been given great support as a result of the material needs of space and advanced aircraft industries. One of the earliest of the thermally stable polymers which could suit this need was the polyimide.

Polymers which possess desirable thermal properties are usually difficult to fabricate into products. Recently prepolymers which are workable before curing have been employed to extend the practical applications of these polymers.

In regard to the imides, commercial polymers are available which

are copolymers of imides. For example, by incorporating the amide linkage, a more processable, soluble, moldable, and usable material is obtained. Copolymerization involves a trade-off with a decrease in thermal stability of the polymer as is shown by the TGA curves in Fig. 1¹. Even so, these copolymers can still withstand use at 290°C for 2000 hours.

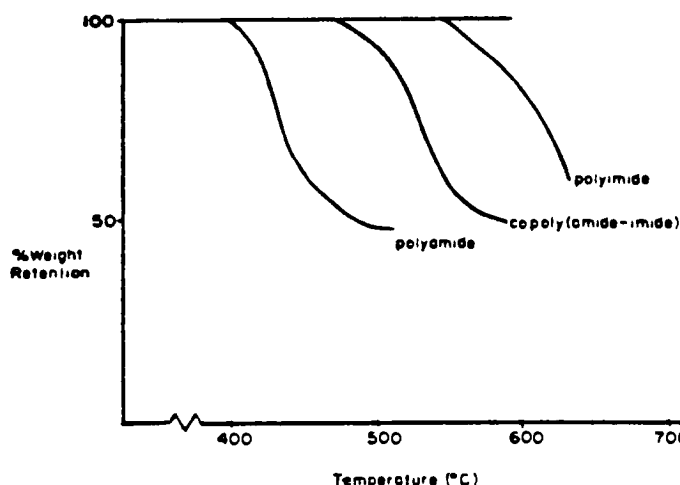


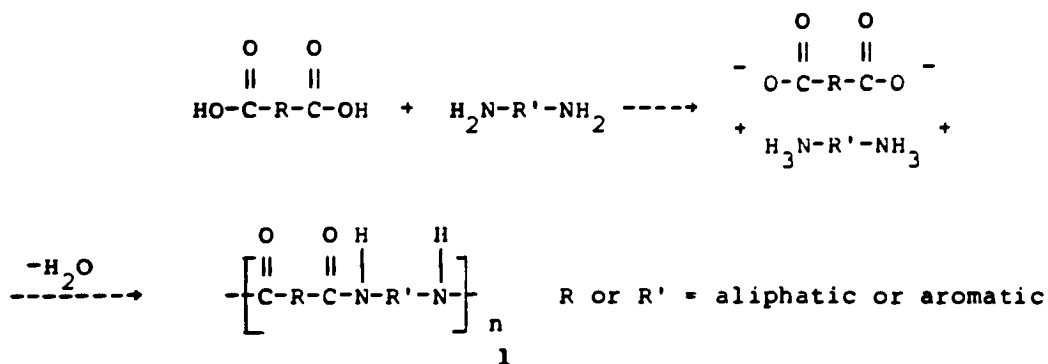
Figure 1 TGA curves showing the effect of amide and imide backbone composition.

In general thermally stable polymers should have the following properties: (a) high melting or softening points; (b) low weight loss as determined by TGA; (c) structures that are not susceptible to degradative chain scission or intra- or intermolecular bond formation; (d) chemically inert especially to oxygen, moisture, and dilute acids and bases. Chemical structures which are thermally stable usually also have (a) a highly resonance-stabilized system; (b) an aromatic or other thermally unreactive ring structure comprising a major portion of the polymer; and (c) a high bond and cohesive energy density.

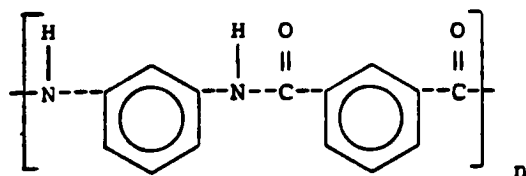
1.1 Polyamides

Polyamides have the general structure of

$$\left[\begin{array}{c} \text{O} \quad \text{O} \quad \text{H} \quad \text{H} \\ \parallel \quad \parallel \quad | \quad | \\ -\text{C}-\text{R}-\text{C}-\text{N}-\text{R}'-\text{N}- \end{array} \right]_n$$
 and can be prepared by the direct interaction of a dicarboxylic acid and a diamine (i.e. melt polymerization) to yield the corresponding polyamide 1.



Polyamides usually exhibit high melting temperatures, for example, the polyamide derived from phenylene diamine and an aliphatic diacid chloride has a melting temperature of over 300°C. The good thermal resistance and toughness of polyamides have lead to many investigations of their thermal properties. A well known polyamide is E. I. du Pont de Nemours Co. Nomex¹, having structure 2,

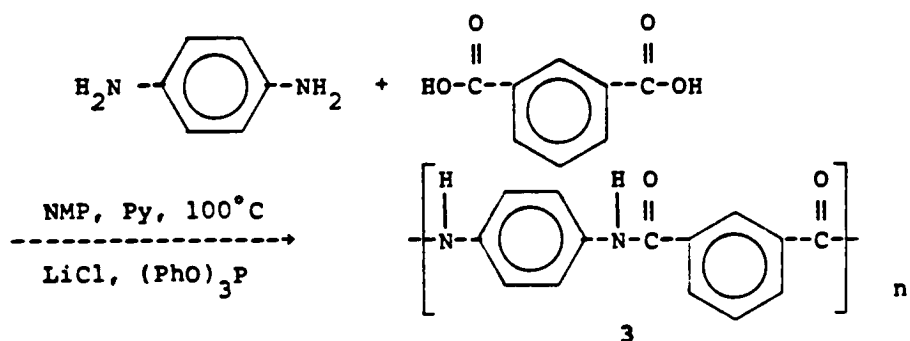


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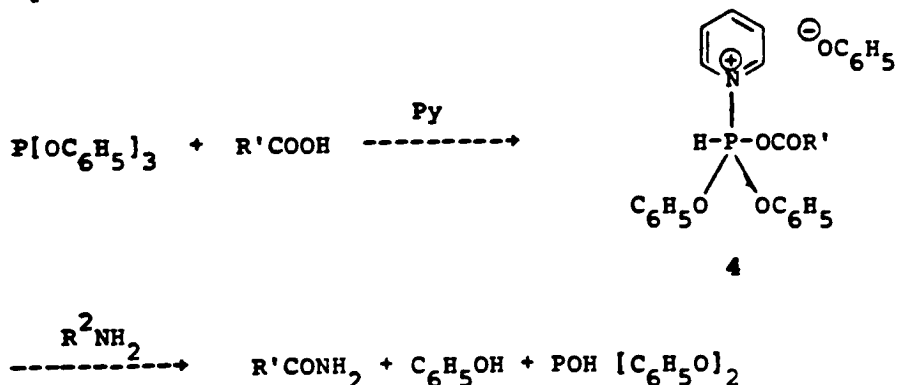
with the meta orientation providing for flexibility. The order of the units along the backbone is extremely important since the melting point can vary 100°C from an ordered to a random arrangement. The decomposition temperature of Nomex is 370°C, and the TGA shows a 10%

weight loss at 450°C. It is interesting to note that if a para orientation is used for polyaromatic polyamides, one witnesses a three to six fold increase in modulus, lower elongation to breakage, increased intractability, more crystallinity, improved thermal stability, higher tensile strength, and lower solubility.

A new method for polyamide synthesis was reported by Yamazaki and co-workers². A high molecular weight polyamide 3 was obtained ($\eta_{inh} = 1.5$ dL/gm in conc. sulfuric acid) when p-phenylene diamine was reacted with isophthalic acid in the presence of triphenyl phosphite, pyridine and lithium chloride.



It is postulated that the reaction proceeded via the N-phosphonium salts 4 of pyridine followed by aminolysis:



Imai and co-workers³ have also prepared various aromatic and

aliphatic polyamides using the Yamazaki reaction. The polymers obtained gave high inherent viscosity values. For example the polymer obtained from the reaction between 4,4'-oxydianiline and terephthalic acid gave an inherent viscosity value of 2.39 dL/gm in concentrated sulfuric acid. Using isophthalic acid, the polymer obtained gave an inherent viscosity value of 1.98 dL/gm, suggesting high molecular weight materials.

Important factors in the Yamazaki reaction are temperature, solvent, monomer concentration, metal salt type and reaction time. The best solvent for this reaction was found to be N-methyl-2-pyrrolidone with the monomer concentration being 0.6 moles per liter.

The results for the polymerization of p-aminobenzoic acid using the Yamazaki reaction are summarized in Table I.

Table I²: Polycondensation Reaction of p-Aminobenzoic^a Acid Using Triphenyl Phosphite in Various Solvent Systems Containing 4% (w/v) Lithium Chloride

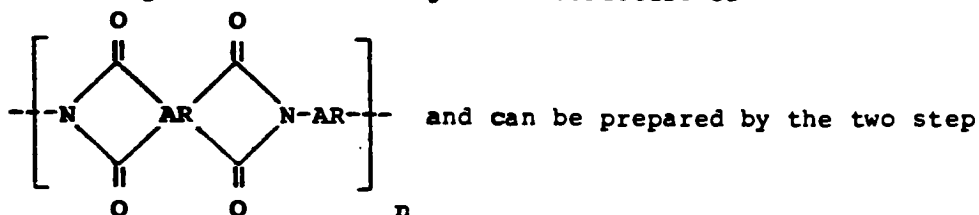
<u>Solvent System</u> (ml/ml)	<u>% Yield</u>	<u>Inherent Viscosity^b</u> (dL/gm) C=0.5 gm/dL
Dioxane/Pyridine (40/10)	21	0.07
DMF/Pyridine (40/10)	11	0.08
DMAC/Pyridine (40/10)	99	0.71
Pyridine (50)	100	0.21
NMP/Pyridine (10/40)	100	0.29
NMP/Pyridine (20/30)	100	1.21
NMP/Pyridine (30/20)	100	1.57
NMP/Pyridine (40/10)	100	1.27
NMP/Pyridine (45/5)	100	1.26

a) Monomer concentration = 0.4 mole, triphenyl phosphite concentration = 1 mole/mole monomer, temperature = 100°C, reaction time = 6 hrs.

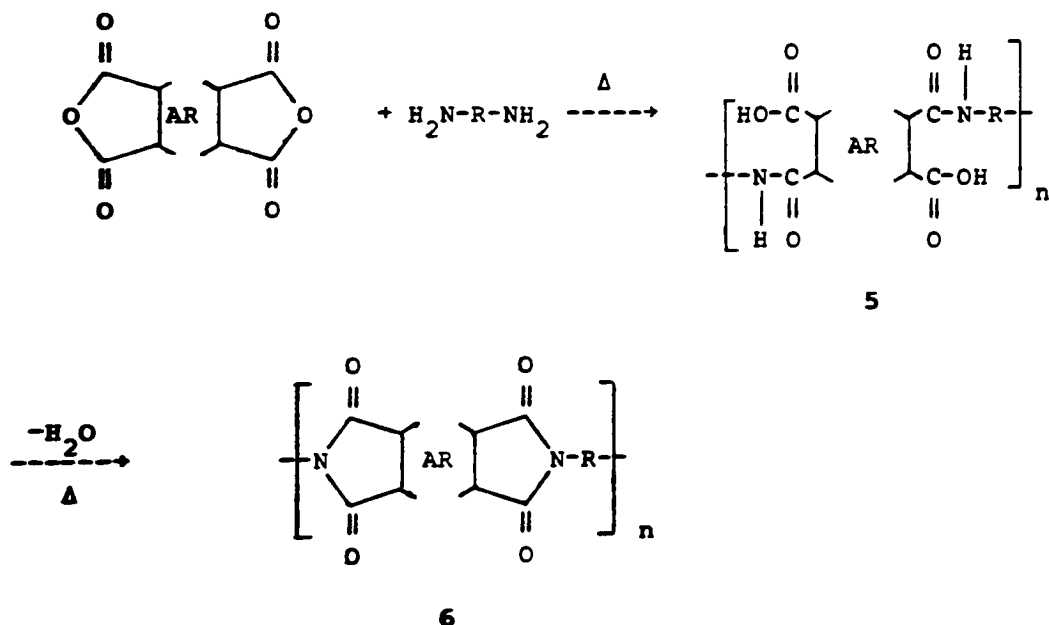
b) Measured in concentrated sulfuric acid at 30°C.

1.2 Polyimides

Polyimides have the general structure of



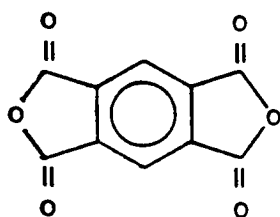
condensation reaction of a dianhydride with a diamine. The first step produces an intermediate polyamic acid 5 which is processable and soluble. The final product conformation is developed at this point (film, fiber, etc.). The post cure process takes place at an elevated temperature to complete the dehydration/ring closure to give polyimide 6 which resulted in a product insoluble in common polymer solvents.



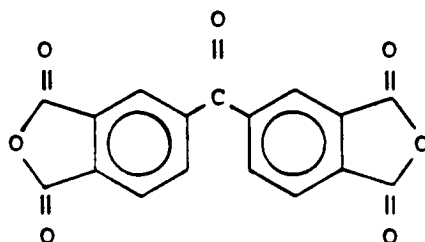
Extensive research to date has converted nearly every conceivable AR and R group for this system. The most common dianhydrides are those

from pyromellitic acid 7 and benzophenone tetracarboxylic acid 8.

Among the diamines are aliphatics, p-phenylene and bridged biphenylene and bipyridyl units, (with methylene, oxygen, and sulfone bridges to provide product flexibility due to chain mobility).

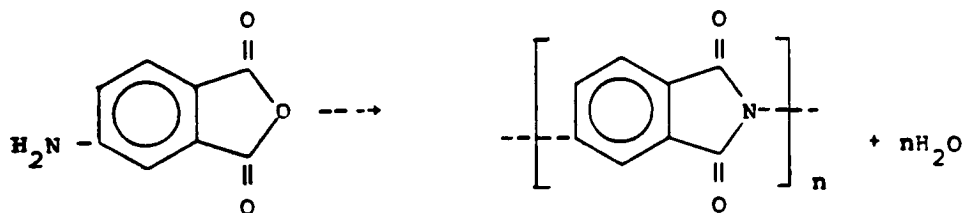


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8

It is interesting to note that polyimides were first reported as early as 1908 by Bogert and Renshaw³, who described the condensation of 4-aminophthalic anhydride to give the polyimide 9.



9

In 1964, Edwards and co-workers⁴ described the conditions of reaction of bis(4-aminophenyl)ether 10 and pyromellitic dianhydride 7, and the data are shown in Table II on page 10.

Table II⁴: Effect of Temperature of Polymerization on Inherent Viscosity of Polyamic Acid
[Reaction of Bis(4-Aminophenyl) Ether and Pyromellitic Dianhydride].

<u>Solvent</u>	<u>10</u> (gm)(mole)	<u>6</u> (gm)(mole)	<u>Solids</u> (%)	<u>Temp.</u> (°C)	<u>Time at Temp.</u> (min.)	<u>η_{inh}</u> ^a
DMAC	10.00 0.05	10.90 0.05	10.0	25	120	4.05
DMAC	10.00 0.05	10.90 0.05	10.0	65	30	3.47
DMAC	20.00 0.10	21.80 0.10	10.6	85-88	30	2.44
DMAC	20.00 0.10	21.80 0.10	10.7	115-119	15	1.16
DMAC	20.00 0.10	21.80 ^b 0.10	10.3	125-128	15	1.00
DMAC	20.00 0.10	21.80 ^c 0.10	15.7	135-137	15	0.59
N-Me caprolactam	10.00 0.05	10.90 0.05	14.2	150-160	2	0.51
N-Me caprolactam	10.00 0.05	10.90 0.05	12.9	175-182	1-2	Partly Soluble
N-Me caprolactam	20.00 0.10	21.80 0.10	15.0	200	1	Insoluble

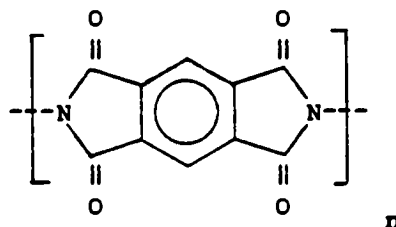
a) Determined at 0.5% concentration in the particular solvent at 30°C

b) Increment of 0.35 gm 6 added before determination of η_{inh} .

c) Increment of 0.25 gm 6 added and then 0.21 gm 10 added before determination of η_{inh} .

Polyimides, cured from polyamic acids, exhibit a variety of properties and characteristics. Polyimides derived from aliphatic diamines show properties generally dependant on the diamine chain. Polyimides derived from aromatic diamines are the most important commercially, because of their outstanding thermal properties. Aromatic polyimides are resistant to radiation, solvent, bacterial attack, acidic hydrolysis, and deformation at elevated temperature. As such, they have recently been found to be excellent hyperfiltration or reverse osmosis membranes after the incorporation of a polar functional group (methoxy, carboxyl, or hydroxyl) onto the backbone. A well known polyimide is E. I. du Pont de Nemours Co.

Kaptan¹ which has structure 11.

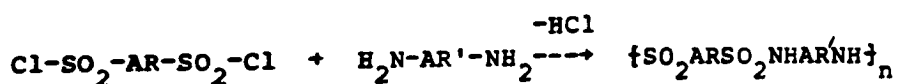


11

Kaptan has an inherent viscosity of 1.19 dL/gm, a Tg greater than 500°C, and showed a 5% weight loss at 325°C for 300 hours¹.

1.3 Polysulfonamides

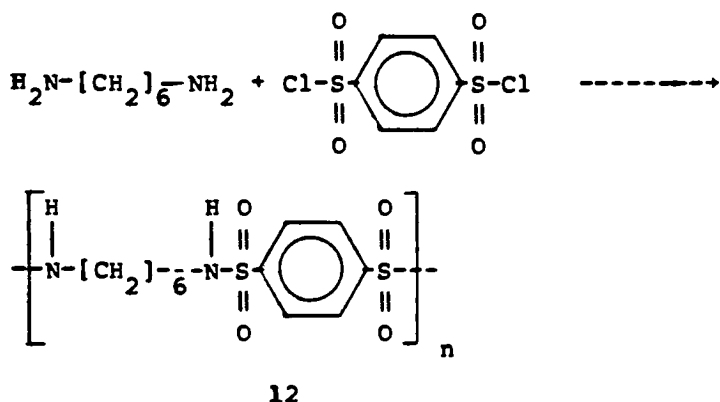
Polysulfonamides have the general structure of $\{R-NH-SO_2-R'\}_n$ and can be prepared by the condensation reactions of aromatic disulfonyl chlorides with diamines.



Polysulfonamides exhibit excellent stability to hydrolysis in both acidic and basic solutions. Unlike polyamides and polyimides, polysulfonamides exhibit low levels of thermal stability. This low

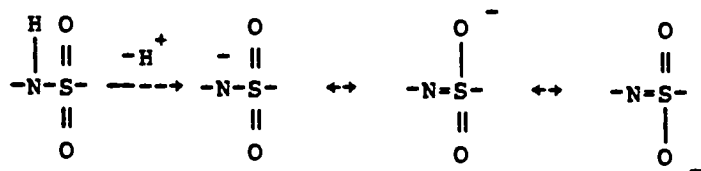
level of thermal stability is offset by exceptional workability, ease of casting, and film forming qualities.

A series of high molecular weight polysulfonamides were prepared from the reaction of an aromatic disulfonyl chloride with various aliphatic diamines by S. A. Sundet and co-workers⁵. An example of this is the reaction of 1,6-hexamethylene diamine with benzenedisulfonyl chloride to form a polysulfonamide 12.



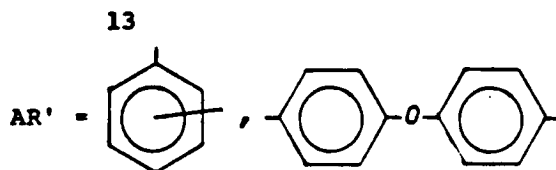
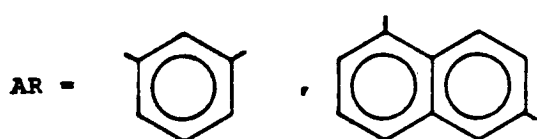
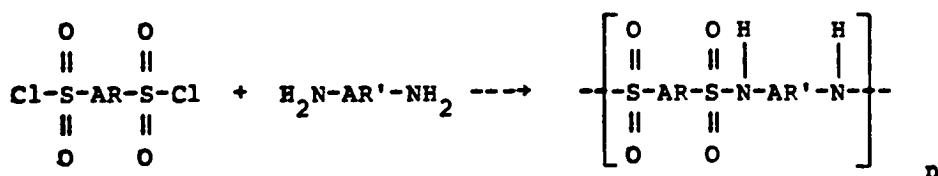
Using an interfacial polymerization technique, polymers with an inherent viscosity ranging from 0.1 to 2.62 dL/gm were obtained. Higher molecular weight polymers were obtained when sodium carbonate rather than sodium hydroxide was used as the acid acceptor. This was attributed to a reduction of the sulfonyl chloride hydrolysis at the lower pH. In addition, the carbonate may be acting to "salt out" the diamine more rapidly into the organic phase.

In the synthesis of polysulfonamides, pH control is important. Sulfonamides dissolve in 10% sodium hydroxide solution because of the acidity of the sulfonamide group.



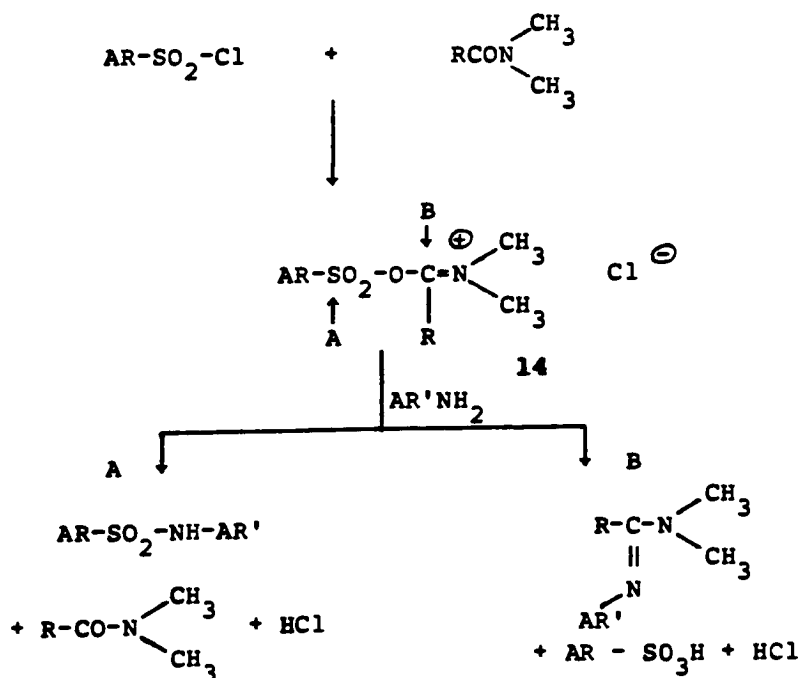
Thus, interfacial polymerizations carried out at higher pH levels cause the formation of the anion ($-\text{SO}_2-\bar{\text{N}}-$) which can be sulfonated in sufficient amounts to form a branched and/or insoluble polymers. This phenomena was observed in the reaction of 1,2-ethylene diamine and 1,3-benzenedisulfonyl chloride, using sodium hydroxide as the acid acceptor.

Sundet and co-workers⁵ were unable to prepare wholly aromatic high molecular weight polysulfonamides due to the low basicity of the aromatic diamines and the lower reactivity of the sulfonyl chlorides as compared to carboxylic acid chlorides. Low molecular weight polysulfonamides 13 were also obtained by C. S. Marvel and his co-workers⁶ by reacting aromatic diamines with aromatic disulfonyl chlorides. The polymers obtained using the solution polymerization technique with N,N-dimethylacetamide or tetramethylene sulfone as the solvents, gave a range of inherent viscosities between 0.02 to 0.19 dL/gm.



Imai and co-workers⁷ were able to synthesize wholly aromatic

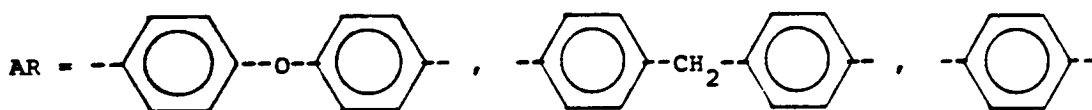
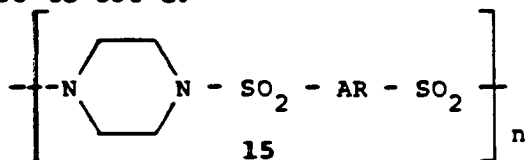
polysulfonamides using a low temperature polymerization technique. Unlike Marvel and co-workers⁶, 2-methyl pyridine was used as the solvent and pyridine as the acid acceptor in their reactions. This combination of solvent and acid acceptor gave a polysulfonamide with an inherent viscosity of 0.43 dL/gm with a 99% yield. The formation of a high molecular weight polymer was attributed to the solvent's ability to sufficiently dissolve or swell the polymer thus permitting complete polymerization. Polymerizations using amide type solvents such as N,N-dimethylacetamide (a good solvent for aromatic polysulfonamides), produced inferior results. Aromatic sulfonyl chlorides are known to react with N,N-dialkylamides to give the ammonium salt 14⁸. The reaction of which, produced a mixture of sulfonamides (through path A) and the imidines (through path B) in the equation shown below.



It was assumed that N,N-dimethylacetamide reacted with the

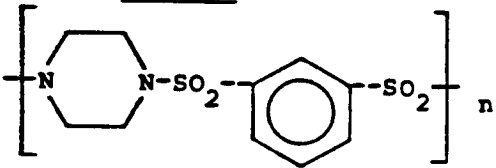
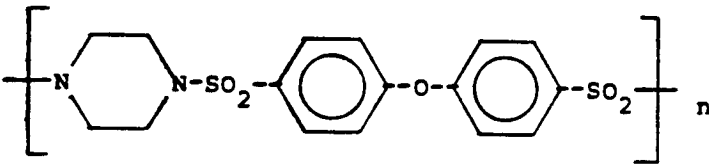
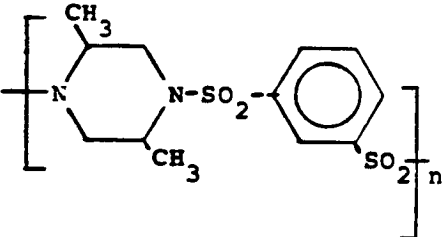
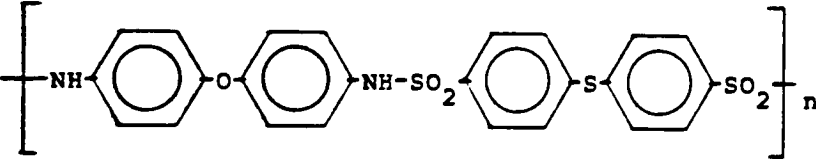
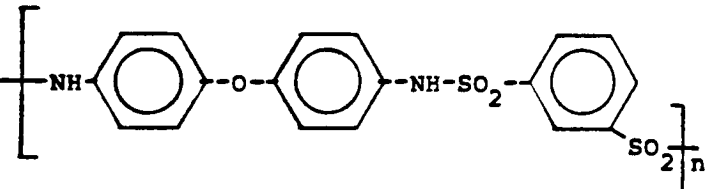
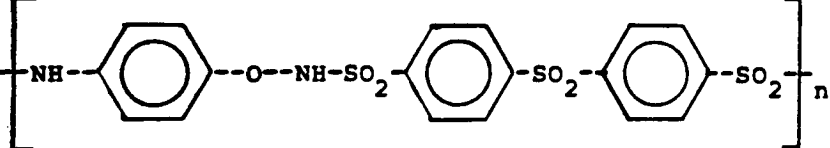
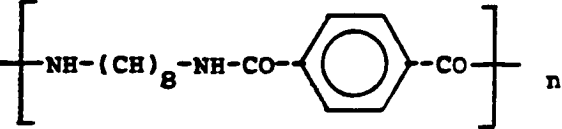
aromatic disulfonyl chlorides to form the sulfonic acids which resulted in the termination of the polycondensation and yielded only low molecular weight polysulfonamides.

In general, aromatic polysulfonamides exhibit lower thermal stability than that of aromatic polyamides. R. C. Evers and G. F. L. Ehlers⁹ found that piperazine aromatic polysulfonamides 15 decomposed around 300 to 350°C.



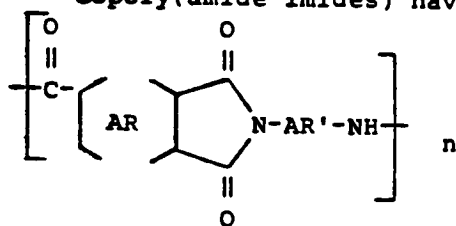
Polyamides showed a higher decomposition temperature of approximately 410 to 450°C¹⁰. The lack of thermal stability shown by polysulfonamides can be attributed to the nitrogen sulfur bonds in the polymer backbone. The thermal stability of polyamides and polysulfonamides are summarized in Table III.

Table III: Thermal Properties of Polyamides¹⁰ and Polysulfonamides⁹
Under Nitrogen Atmosphere

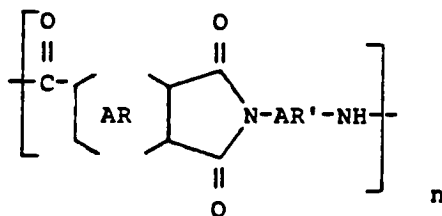
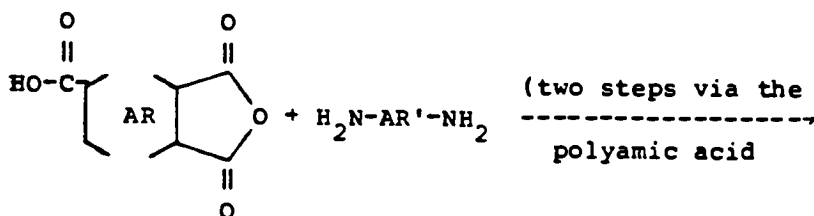
<u>Polymer</u>	η_{inh}	<u>TGA(°C)</u>
	0.07	350
	0.12	355
	0.07	310
	0.25	400
	1.27	380
	0.40	395
	N/A	470

1.4 Copoly (amide-imides)

Copoly(amide-imides) have the general structure of



and can be prepared by the reactions of trimellitic acid chloride and various diamines. As in the case of the polyimide the copoly(amide-imide) 16 is usually prepared from the intermediate polyamic acid.



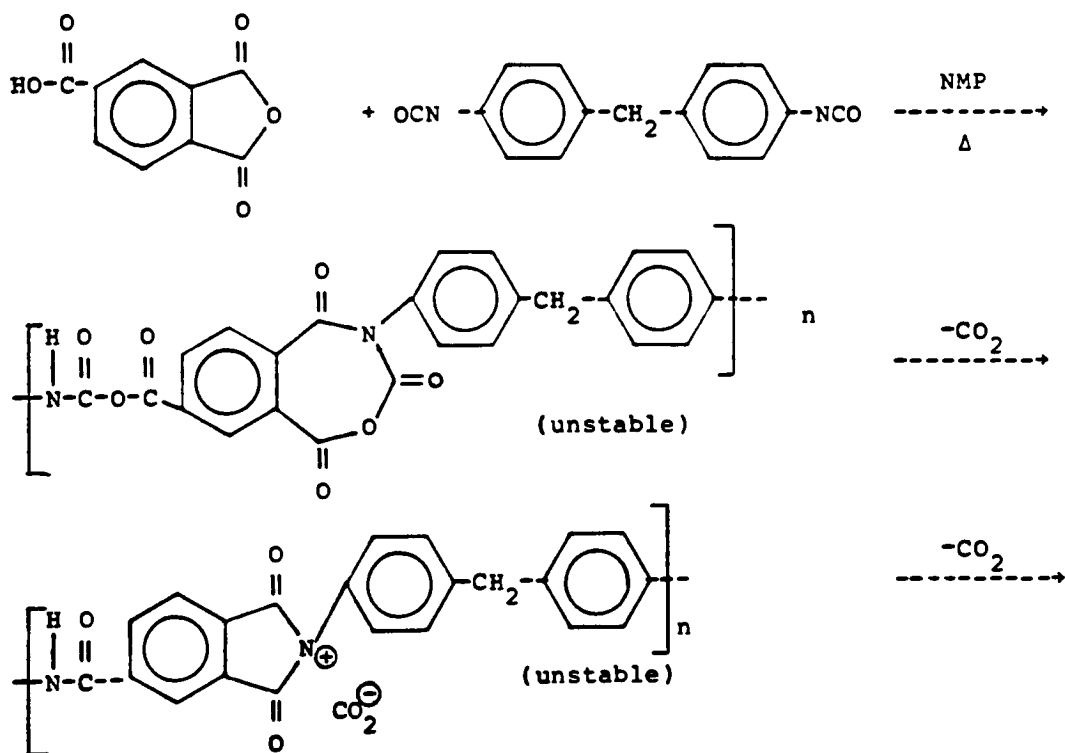
16

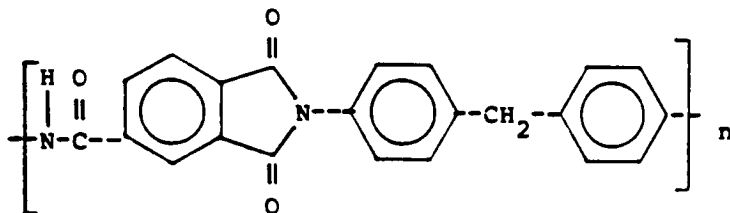
By polymerizing the two functionalities of the amide and imide into the backbone of the macromolecule a polymer of intermediate properties would be obtained. Incorporating the amide linkage into a polyimide it was believed that it would be possible to obtain the best properties of each monomer unit (i.e, more processable, soluble, and moldable). Thus, the brittle, thermally stable, inert polyimide was converted to a thermally stable yet workable polymer.

Leaving groups other than chloride were investigated but with much less success. The acid and imidazol functions were found to

react at a lower rate and higher temperatures and to give lower yields than the chloride. Of course, again, these reactions occur with production of the intermediate polyamic acid which must be thermally cyclized.

A unique method to synthesize a copoly(amide-imide) was shown by S. Terney and co-workers¹¹. Reaction of trimellitic anhydride with aromatic diisocyanates, a function more reactive than a diamine, results in the reaction of the diisocyanate with both the carboxylic acid and the anhydride¹² with subsequent loss of carbon dioxide to give a copoly(amide-imide) 17. Note that due to the reactivity of the isocyanate, no second curing step is needed for imide formation.





17

By the partial replacement of the triacid with an aromatic diacid or tetraacid dianhydride, the amide or imide content respectively could be increased. It is no surprise that increased imide function leads to better thermal stability. However, upon deviation from the 50:50 functional group molar ratio, the polymer solution developed instability in terms of viscosity. This was postulated as due to a slow aggregation of amide functions by hydrogen bonding.

The thermal stabilities ranged from 485 to 565°C with a direct relationship to the imide content of the copolymer. Specifically, the polymer with 20 mole % terephthalic acid showed the least thermal stability, while that with 100% pyromellitic acid was the most thermally stable. It is of interest to note that the ideal ratio, i.e. 50:50, amide to imide linkages, is only approximately 5°C more thermally stable than the copolymer consisting of 20% terephthalic acid, which is at the low end of the thermal stability scale.

Polyamic acids are inherently hydrolytically unstable and undergo hydrolysis during preparation, storage and cyclization. To avoid the problem of crosslinking during the cyclization step, W. Wrasidlo and J. M. Augl¹³ employed low temperature solution condensations of aromatic diamines and bifunctional carboxylic acid

chlorides. These carboxylic acid chlorides contained preformed imide linkages and were used to synthesize the copoly (amide-imides) 18.

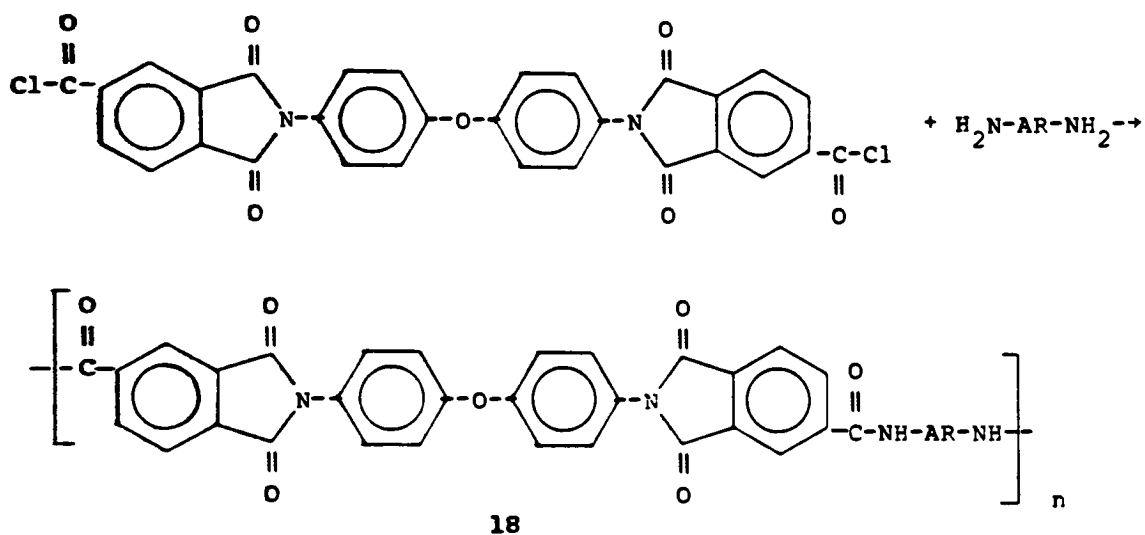

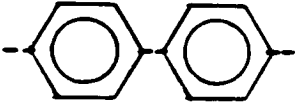
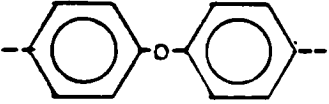
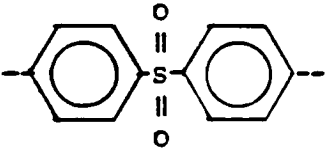


Table IV gives the resultant properties of these copolymers with four different AR groups incorporated into the backbone.

Table IV¹³: Properties of Copoly (amide-imides).

<u>AR</u>	<u>Solubility in DMAc</u>	<u>[η]^a</u>	<u>T_g(°C)^b</u>	<u>PDT(°C)^{c, f}</u>
	Insoluble ^d	0.7	--	455
	Insoluble ^d	0.9	315	520
	Soluble ^e	2.0	290	460
	Soluble ^e	1.6	275	475

a) Determined in DMAc at 30°C.

b) From dielectric loss measurements.

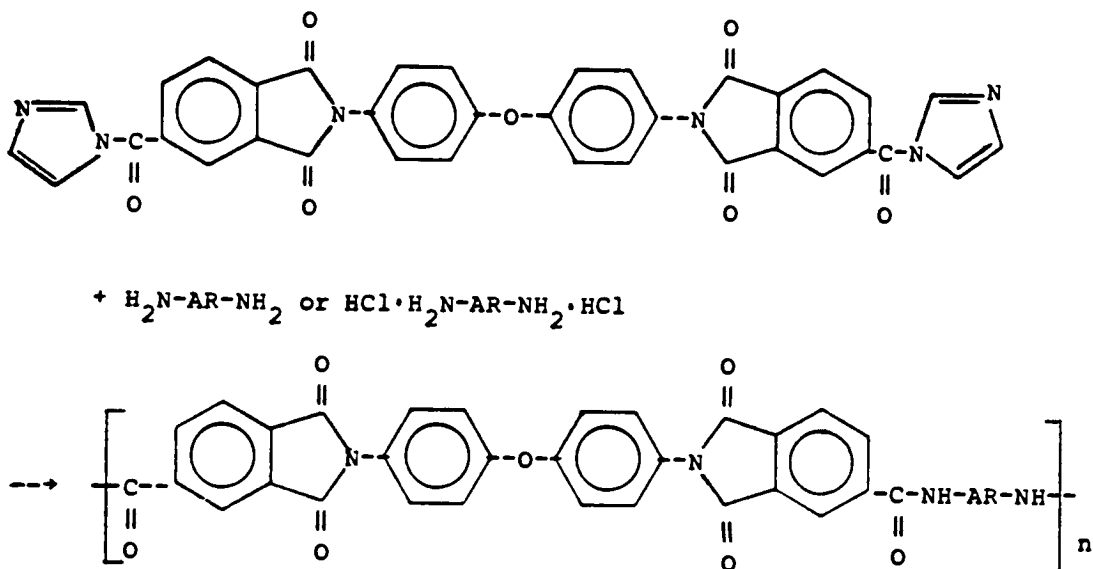
c) By thermogravimetric analysis in vacuum at a heating rate of 5°/min.

d) Soluble in DMAc + 5-10% lithium chloride.

e) In concentrations up to 30% solids.

f) P.D.T. = polymer decomposition temperature.

In contrast, F. Hayno and H. Komoto¹⁴ prepared and polymerized the diimidazolidine containing preformed imide linkages, shown below, with various diamines to yield copoly (amide-imide) 19.

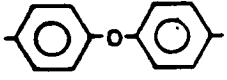
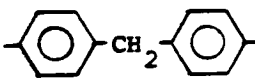
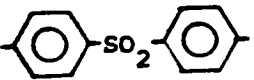


19

The reaction between the diimidazolidine and 4,4'-oxydianiline was carried out at 130°C. The diimidazolidine dissolved gradually as the reaction proceeded, and a viscous solution was obtained. When the reaction was carried out at room temperature, the diimidazolidine remained undissolved.

Dihydrochlorides of the diamines reacted more rapidly with the diimidazolidine, even at room temperature, and high molecular weight copoly(amide-imides) were obtained. When the reaction of the diimidazolidine with the dihydrochlorides of 4,4'-oxydianiline or 4,4'-methylenedianiline was carried out in *N,N*-dimethylacetamide at high concentrations, gelation occurred. Table V shows a summary of these results.

Table V¹⁴: Properties of Copoly(amide-imides).

Exp ^a	R	Conc. ($\frac{\text{mmole}}{\text{ml}}$)	Temp ^b (°C)	Time (min.)	Yield (%)	η_{inh} ^c
A		5/15	130	5	Gelation	--
A		5/20+20 ^d	130	15	105	0.21
H		5/20	50 RT	5 40	Gelation	--
H		5/20+20 ^d	40 RT	10 20	101	0.74
H		5/20+20 ^d	RT	150	100	0.35
H		5/20	45	120	101	0.33
H		5/20	90	60	101	0.34
H		5/20	RT	150	101	0.29
H		5/20	90	30	103	0.28
H		5/20	RT	150	104	0.21

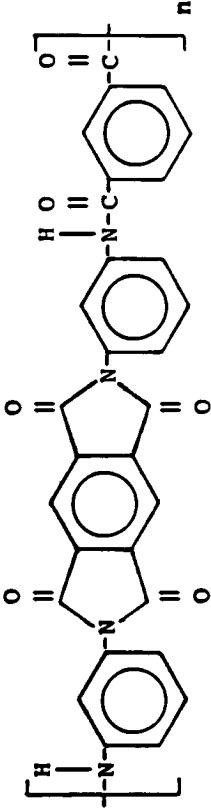
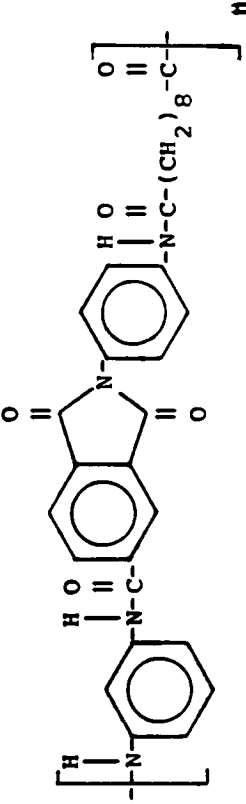
- a) A: diamine monomer; H: hydrochloride of diamine monomer.
b) RT = room temperature.
c) Concentration = 0.5gm/100ml in DMAc at 30°C.
d) A 20ml portion of solvent was added in the course of the polymerization.

Following the lead of Wrasidlo and Augl, W. M. Alvino and L. W. Frost¹⁵ reacted diamines, containing the preformed imide linkage, with diacid chlorides to yield the copoly(amide-imides) shown in Table VI.

Table VI¹⁵, Properties of Selected Copoly(amide-imides).

<u>Repeating Unit</u>	<u>TGA (°C)</u>	η_{inh}^a $\frac{dL}{gm}$
	~440	1.09
	~450	1.17
	~420	0.79

Table VI¹⁵: Properties of Selected Copoly(amide-imides). (Continued)

<u>Repeating Unit</u>	<u>TGA (°C)</u>	η_{inh}^a	$\frac{dL}{dm}$
	-----	-----	-----
	~400	1.13	

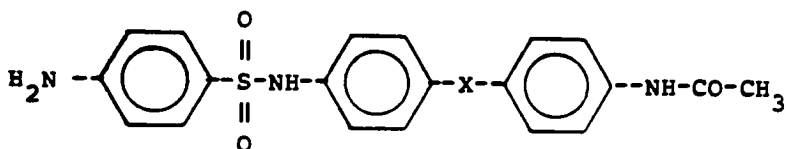
a) 0.5% in DMAC

These polycondensation reactions proceeded very rapidly and exothermally, and it was found necessary to add the acid chloride slowly to avoid gelation at high solids concentration. The viscosity of the solution increased to a maximum in about 20 minutes, whereas polyamic acids prepared from diamines and dianhydrides usually reach maximum viscosity only after several hours. Polymerization at high dilution produced polymers of low inherent viscosity.

Alvino and Frost¹⁵ also found that the use of propylene oxide instead of pyridine as the acid acceptor enabled them to cast creasable films directly from the reaction mixture. This may be due to the propylene oxide acting as a plasticizer. Films cast from the reaction mixture containing pyridine were brittle. In the case such as this, precipitation and thorough washing of the polymer was necessary before flexible films could be obtained. After aging six months at room temperature no decrease in viscosity was observed. Thick films could be cast from solution without the degradation common to the polyamic acid precursors of conventional polyimides.

2.0 OBJECTIVE

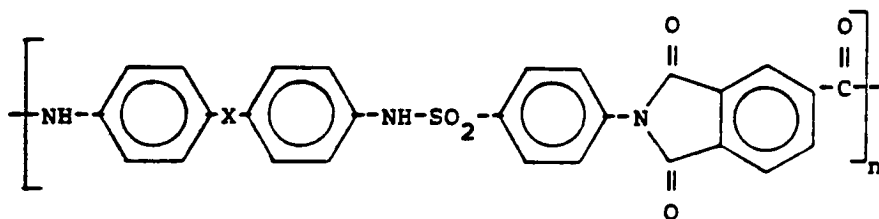
The first aim of this research project was the synthesis of the amino-sulfonamido-acetanilide monomers 20 and 21 in greater yields and subsequent separation-purification by a more efficient means than had been achieved by previous workers.



20 where x = $-\text{CH}_2-$

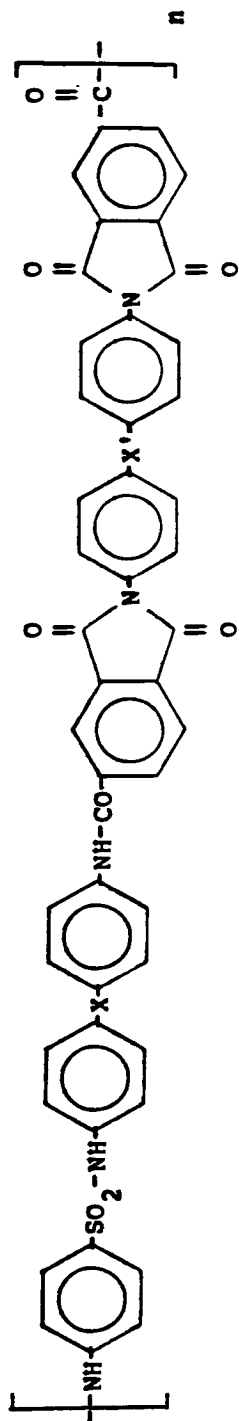
21 where x = $-\text{O}-$

The second aim of this research project was the synthesis and characterization of a series of novel copoly (amide-imide-sulfonamides), having the structure 22 shown below, using low temperature solution polymerization techniques.

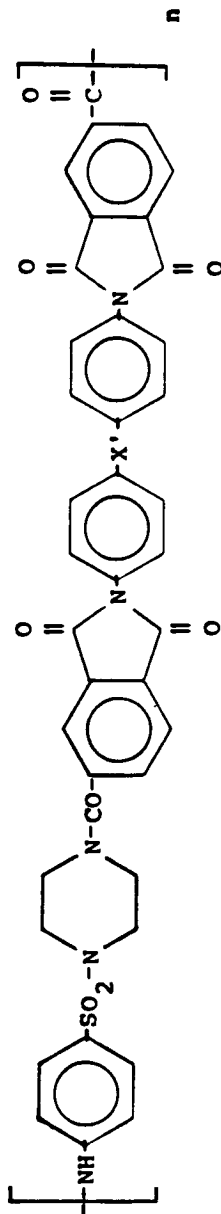


22
where x = $-\text{O}-$, $-\text{CH}_2-$

Polymerizations were then undertaken utilizing the Yamazaki reaction². In the Yamazaki reaction, under the conditions specified, the reaction of an anhydride with a diamine resulted in a highly crosslinked material. It was then that the aim of this project was changed to the preparation of copoly(amide-imide-sulfonamides) having the general structure of 23 and 24, where one monomeric unit contained a preformed imide linkage.



23



24

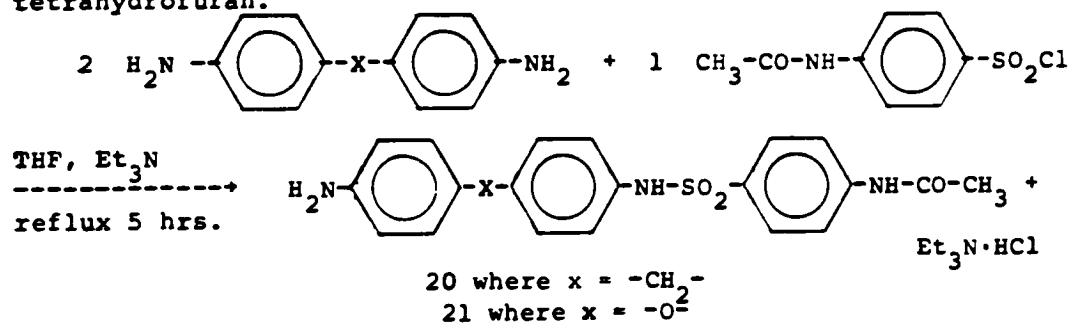
where $x = -CH_2-$, $-O-$

where $x' = -CH_2-$, $-O-$, $-CH_2CH_2-$

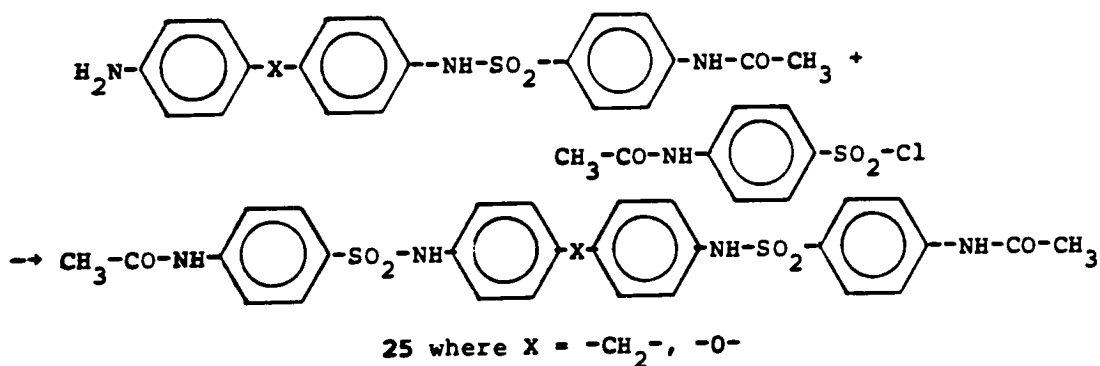
Once synthesized, these polymers would be characterized by dilute solution viscosity, infrared spectroscopy, thermal gravimetric analysis and differential scanning calorimetry.

3.0 RESULTS AND DISCUSSION OF DIAMINE MONOMER SYNTHESIS, SEPARATION AND PURIFICATION.

The blocked one to one amino-sulfonamido-acetanilides 20 and 21 were prepared by reacting commercially available diamines such as 4,4'-oxydianiline and 4,4'-methylenedianiline with N-acetamidobenzenesulfonyl chloride, using triethylamine as the acid acceptor, in a two to one stoichiometric ratio in refluxing tetrahydrofuran.



Since the desired amino-sulfonamido-acetanilides 20 and 21 contain a free amine group, they can further react with N-acetamidobenzenesulfonyl chloride to form an undesired amino-sulfonamido-diacetanilide 25, i.e.:



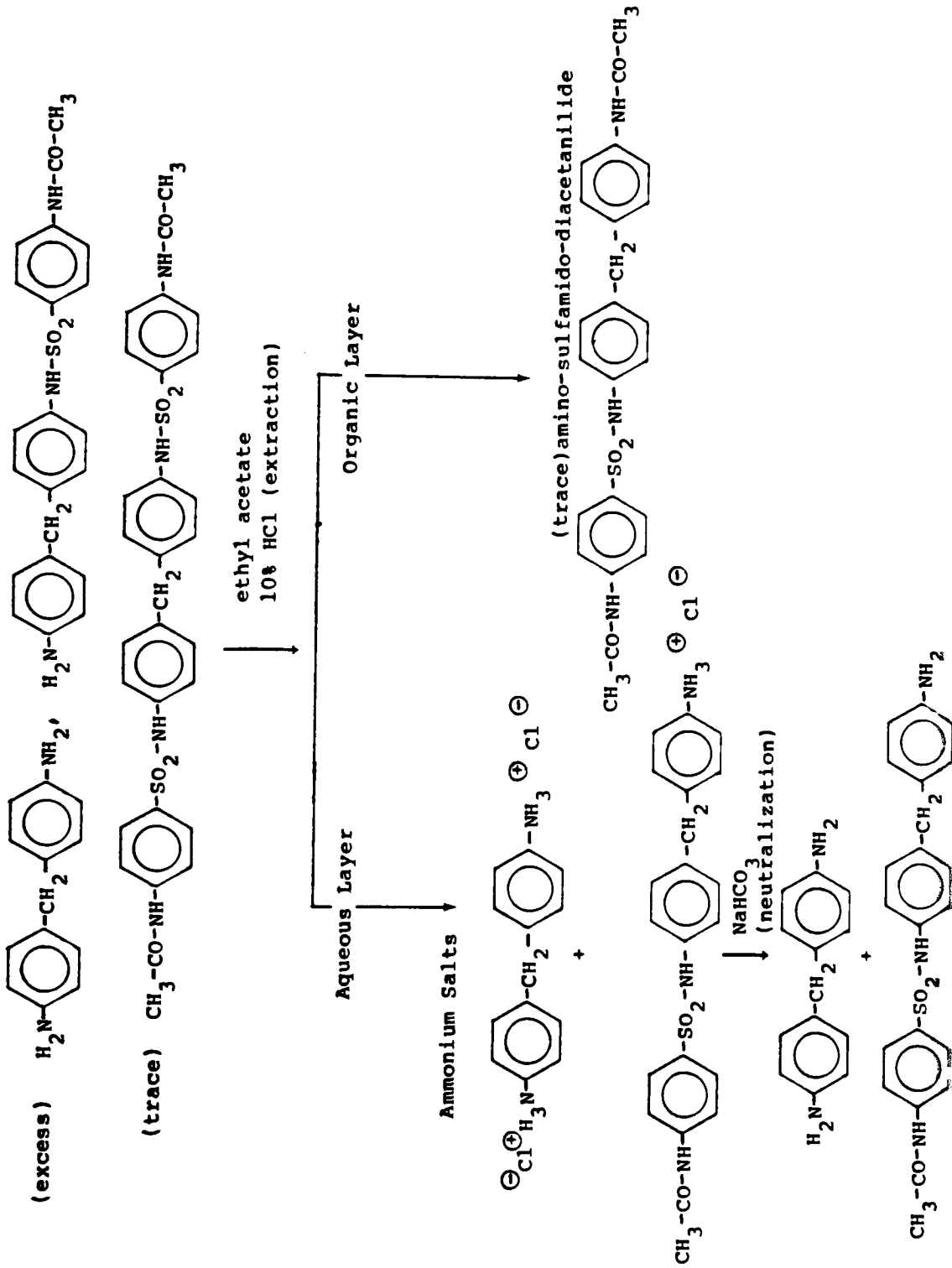
The first goals of this project were to a) decrease or totally eliminate the formation of the amino-sulfonamido-diacetanilide, b) to improve yields of the amino-sulfonamido-acetanilide, and c) to

develop a more time efficient chemical separation-purification technique for obtaining the desired products 20 and 21.

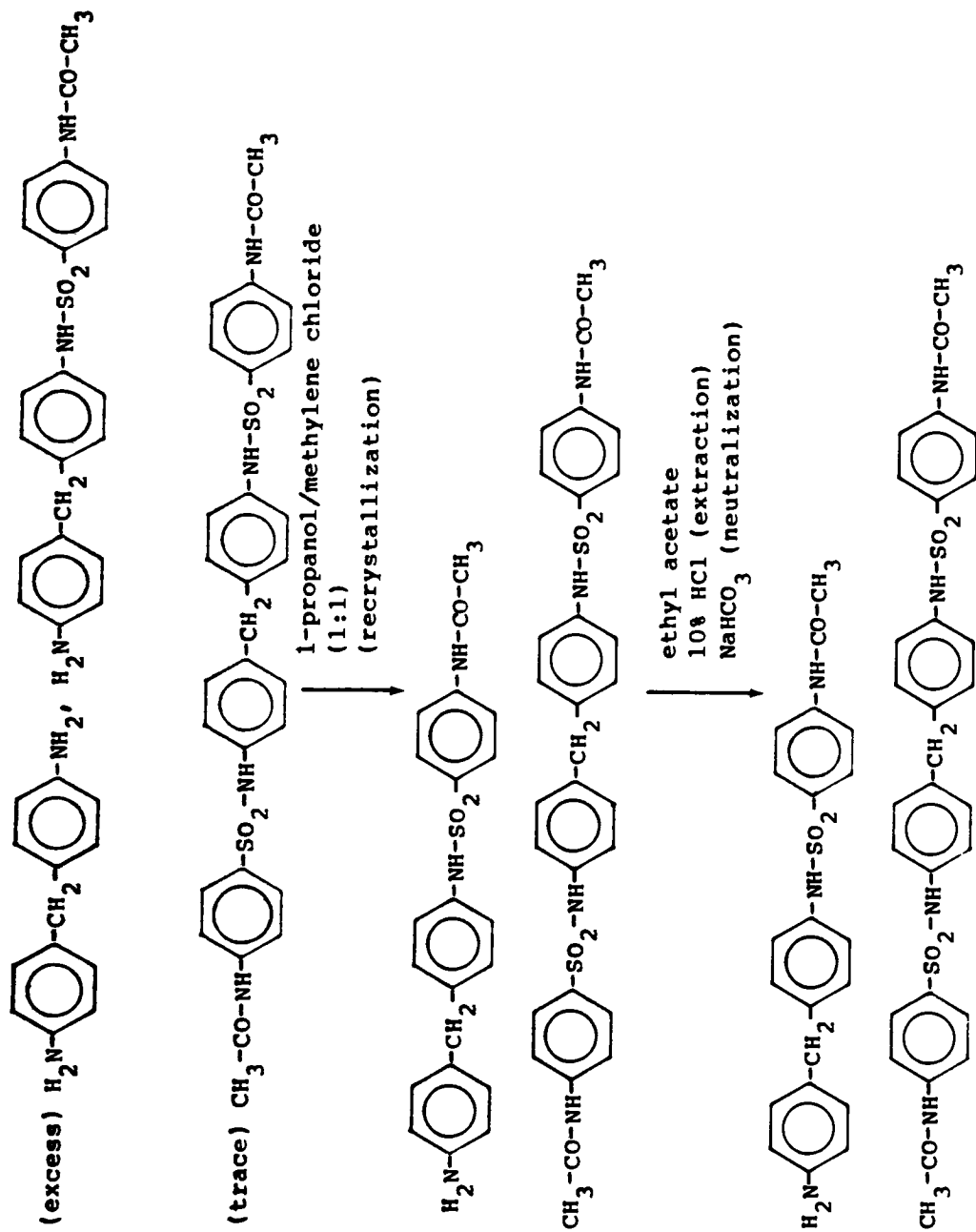
First, a method for the chemical separation-purification of the amino-sulfonamido-acetanilides was investigated according to scheme shown on the next page. The amino-sulfonamido-acetanilide of 4,4'-methylenedianiline was prepared and approximately two grams of the product (4,4'-methylenedianiline, amino-sulfonamido-acetanilide and amino-sulfonamido-diacetanilide) was dissolved in ethyl acetate and then extracted with 10% hydrochloric acid to form the ammonium salt of the amino-sulfonamido-acetanilide and 4,4'-methylenedianiline. Neutralization with sodium bicarbonate gave a tar-like substance which by thin layer chromatography (ethyl acetate/hexanes/acetone (2:1:1)) was shown to be the amino-sulfonamido-acetanilide and 4,4'-methylenedianiline.

According to the scheme given on page 33 another sample of the reaction material containing 4,4'-methylenedianiline, amino-sulfonamido-acetanilide, and amino-sulfonamido-diacetanilide was then recrystallized utilizing various organic solvents. A mixed solvent of 1-propanol and methylene chloride, in approximately equal volume, was eventually chosen and resulted in the removal of the starting material, 4,4'-methylenedianiline, from the amino-sulfonamido-acetanilide and the amino-sulfonamido-diacetanilide as shown by thin layer chromatography.

Reaction Mixture



Reaction Mixture



As shown on the previous page, an attempt was then made to separate the resultant mixture of amino-sulfonamido-acetanilide and amino-sulfonamido-diacetanilide obtained from the recrystallization. The solid material recovered from the recrystallization was dissolved in ethyl acetate and had added to it 10% hydrochloric acid, stirred for a period of time, separated in a separatory funnel, and the aqueous layer was neutralized with sodium bicarbonate. No solid material was obtained after neutralization and upon removing solvent from the organic layer a crystalline substance was obtained which by thin layer chromatography (ethyl acetate/hexanes/acetone(2:1:1)) was shown to be the amino-sulfonamido-acetanilide and amino-sulfonamido-diacetanilide. Also, using the above method with 25% hydrochloric acid the same results were obtained. It thus seemed apparent that once the starting material, 4,4'-methylenedianiline, was removed from the reaction mixture by recrystallization, the ammonium salt formation would not work to further separate the amino-sulfonamido-acetanilide and amino-sulfonamido-diacetanilide. Further experimentation proved that the opposite was also true, i.e., that first treatment of the reaction mixture with 10% hydrochloric acid would separate the amino-sulfonamido-acetanilide and 4,4'-methylenedianiline from the amino-sulfonamido-diacetanilide, but subsequent recrystallization using various organic solvents would not separate the amino-sulfonamido-acetanilide from the 4,4'-methylenedianiline.

The preparation of the amino-sulfonamido-acetanilide involved dropwise addition of N-acetamidobenzenesulfonyl chloride to a

vigorously stirred refluxing solution of the diamine in tetrahydrofuran for a period of approximately two hours. A low concentration of N-acetamidobenzenesulfonyl chloride was maintained to reduce the formation of an unwanted amino-sulfonamido-diacetanilide.

In an effort to decrease the amount of amino-sulfonamido-diacetanilide formed, a reaction was run using a molar ratio of 4,4'-methylenedianiline and N-acetamidobenzenesulfonyl chloride of four to one, respectively, instead of two to one. Attempted separation of the 4,4'-methylenedianiline, amino-sulfonamido-acetanilide and amino-sulfonamido-diacetanilide by ammonium salt formation and recrystallization was not successful. Separation was established by column chromatography using (ethyl acetate/hexanes/acetone (2:1:1)) as the eluent, but a very poor yield (<20%) of the amino-sulfonamido-acetanilide was obtained.

The incomplete solution of N-acetamidobenzenesulfonyl chloride in tetrahydrofuran, causing poor reagent dispersal, was thought responsible for low yields of the amino-sulfonamido-acetanilide obtained. Various new solvents were explored as reaction media. Four solvents were chosen as possibilities: pyridine, N,N-dimethylformamide, N,N-dimethylacetamide, and N-methylpyrrolidone. Neither the N-methylpyrrolidone or the N,N-dimethylacetamide completely dissolved the N-acetamidobenzenesulfonyl chloride upon heating. Both pyridine and N,N-dimethylformamide completely dissolved the N-acetamidobenzenesulfonyl chloride at room temperature, but since pyridine was also an acid acceptor, it was

chosen as the reaction solvent.

The reaction was run using a two to one molar ratio of 4,4'-methylenedianiline to N-acetamidobenzenesulfonyl chloride with pyridine as the reaction medium. Thin layer chromatography (ethyl acetate/hexanes/acetone(2:1:1)) after complete reaction shows the presence of 4,4'-methylenedianiline and a compound with an R_f value intermediate between what was expected for the amino-sulfonamido-acetanilide and the amino-sulfonamido-diacetanilide. Separation-purification by recrystallization and extraction-salt formation was not successful. Column chromatography (ethyl acetate/hexanes/acetone (2:1:1)) was utilized to separate the products of the reaction. A very poor yield (<10%) of the amino-sulfonamido-acetanilide was obtained under these reaction conditions. A homogeneous solution of N-acetamidobenzenesulfonyl chloride in pyridine did not favorably improve the yield of the amino-sulfonamido-acetanilide.

At this point in the project it was realized that separation-purification by recrystallization and extraction-salt formation would not prove to be an efficient method to use. Future separations were conducted by the sole use of dry column chromatography.

The last reaction variable examined in this study was the temperature. It was believed that strict temperature control would reduce the formation of the amino-sulfonamido-diacetanilide. A reaction was carried out keeping the temperature between 58°-61°C. Thin layer chromatographic analysis of the reaction mixture showed the presence of 4,4'-methylenedianiline, amino-sulfonamido-acetanilide, and amino-sulfonamido-diacetanilide. The components of

the reaction mixture were separated using column chromatography (hexanes/ethyl acetate/acetone(3:2:1)) as the eluting solvent. A pure amino-sulfonamido-acetanilide was obtained in yields better than previously reported. Table VII summarizes the results of the synthesis of the amino-sulfonamido-acetanilides.

Table VII: Summary of Amino-Sulfonamido-Acetanilide Synthesis.

<u>X</u>	<u>m.p. (°C)</u>	<u>% Yield^a</u>	<u>R_f^b</u>
-CH ₂ -, 20	171-181	56(48)	0.41
-O-, 21	202.5-208	63(46)	0.42

a) Previously reported yields are given in parenthesis.

b) Eastman chromatogram sheet (13181 silica gel), with ethyl acetate/hexanes/acetone (2:1:1) as the eluent.

The infrared spectra of 20 and 21 showed the characteristic C=O absorptions at $\nu = 1680$ and 1675 cm^{-1} and the N-H absorptions at $\nu = 3340$ and 3220 cm^{-1} , respectively.

The acetyl protecting group of the amino-sulfonamido-acetanilide was removed by treating it with 6M hydrochloric acid under reflux conditions for one-half hour. Deblocking gave the diamino-sulfonamido monomers 26 and 27 in good yield. All the reactions for removing the acetyl protecting group were monitored by thin layer chromatography using (ethyl acetate/hexanes/acetone (2:1:1)) as the eluent. The infrared spectra of the deblocked amino-sulfonamido monomers obtained showed the disappearance of the carbonyl band at $\nu = 1680$ and 1675 cm^{-1} for 20 and 21, respectively.

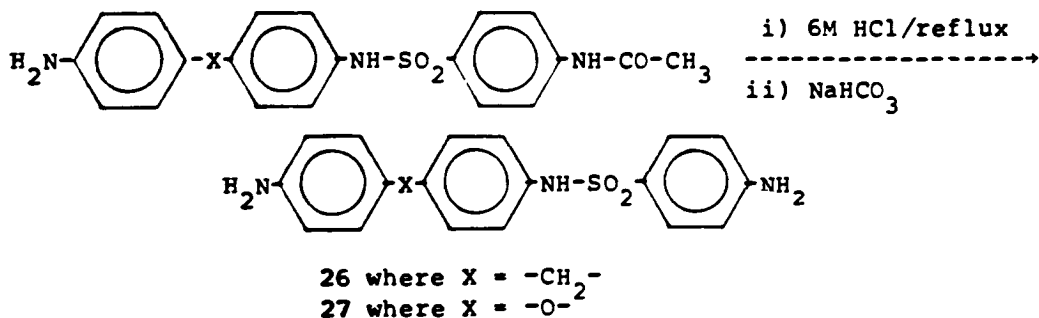


Table VIII summarizes the results of the deblocking reaction on the amino-sulfonamido-acetanilides.

Table VIII: Summary of Deblocking Reaction on Amido-Sulfonamido-Acetanilides.

<u>X</u>	<u>m.p. (°C)</u>	<u>% Yield</u>	<u>R_f^a</u>
-CH ₂ -, 26	174-175	77	0.65
-O-, 27	143.5-144	65	0.66

a) Eastman chromatogram sheet (13181 silica gel), with ethyl acetate/hexanes/acetone (2:1:1) as the eluent.

The deblocked diamino-sulfonamido monomer 26 was then further purified by column chromatography using (hexanes/ethyl acetate/acetone (3:2:1)) as the eluent, and recrystallization from absolute methanol before any polymerizations were attempted. The deblocked diamino-sulfonamido monomer 27 was also purified by column chromatography using the previous mobile system, and recrystallized from isopropanol before it was utilized in any polymerization reactions.

In preliminary deblocking experiments, yields of less than fifty percent were obtained with a one hour reflux time. In order to improve the yield the reaction time was increased to twenty-four hours. Complete deblocking was assumed to have occurred, as shown by thin layer chromatographic analysis. Purifying this monomer and using it in polymerization reactions gave polymers having low inherent viscosities. This monomer was experimentally¹³ predicted to give polymers with the highest viscosities. A melting point of the supposed monomer 27 was found to be approximately twenty degrees lower than the literature value and corresponded with the literature melting point of 4,4'-oxydianiline. An ¹H NMR spectrum of this compound was found to be the same as that of 4,4'-oxydianiline. It was concluded that a twenty-four hour reflux of the amino-sulfonamido-acetanilide in 6M hydrochloric acid at first hydrolyzes the acetyl group, then the sulfonamide linkage to give the starting diamine, 4,4'-oxydianiline. This also explains the low yield of the diamino-sulfonamido monomer obtained when reflux time was one hour. This experimental error occurred because both the deblocked diamino-

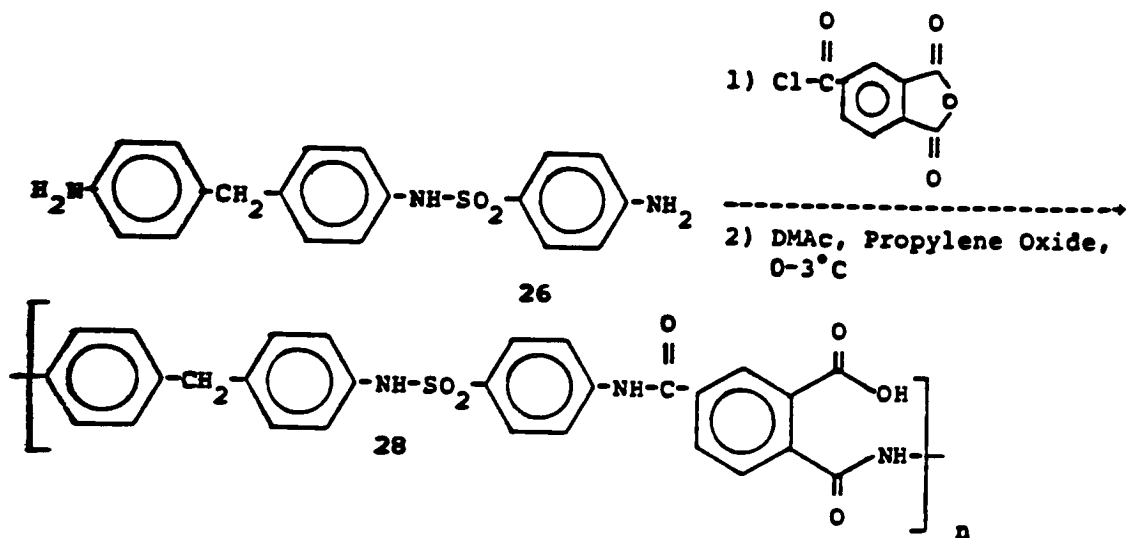
sulfonamido monomer 27 and the blocked amino-sulfonamido-acetanilide 21 had similar Rf values.

Thus, only one part of the first objective in this project was met, that being the preparation of the blocked diamine monomers 20 and 21 in greater yields than had been previously reported. A more efficient chemical means for the separation-purification of the deblocked diamine monomers 26 and 27 could not be found, therefore separations were performed using the technique of dry column chromatography.

4.0 RESULTS AND DISCUSSION OF POLYMERIZATIONS AND THERMAL EVALUATIONS.

The synthesis of the title polymers involved:

- (a) synthesis of an amino-sulfonamido-acetanilide containing a preformed sulfonamide linkage.
- (b) deblocking of the amino-sulfonamido-acetanilide to yield the diamino-sulfonamido monomers.
- (c) solution polymerization of the diamino-sulfonamido monomers with the appropriate anhydride or derivative to form the copoly (amide-imide-sulfonamides). The reaction of trimellitic acid anhydride and monomer 26 using a low temperature solution polymerization with anhydrous N,N-dimethylacetamide and an acid acceptor, propylene oxide, was attempted. The reaction temperature was maintained at 0-3°C for six hours and then overnight at room temperature. The inherent viscosity of the polyamic acid product 28 recovered from this reaction was found to be 0.08 dL/gm. This low viscosity indicates a low molecular weight material.

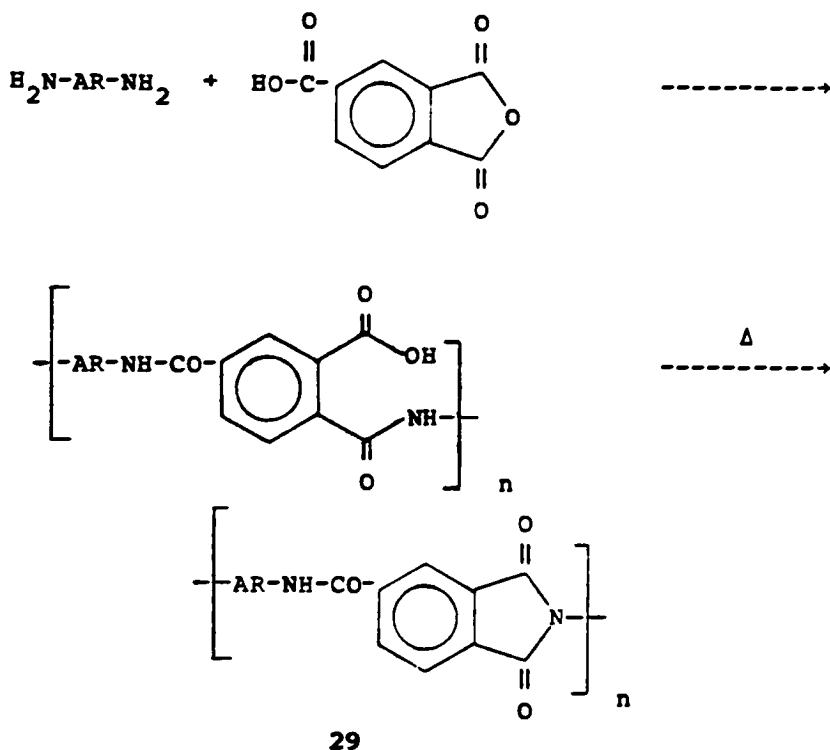


The low molecular weight of 28 may be attributed to a sodium bicarbonate contamination, as shown by thin layer chromatography, of the diamine monomer utilized. This contamination would cause a nonequivalency of functional groups, thus lowering the probability that a high molecular weight polymer could be obtained. High molecular weight polymers can be obtained only if the following requirements are met: (a) high monomer purity, (b) an exact equivalence of functional groups, (c) high reaction conversion, and (d) an absence of side reactions.

Propylene oxide was used as the acceptor instead of pyridine in this polymerization reaction because of results obtained by Alvino and Frost.¹⁵ The use of propylene oxide instead of pyridine enabled them to cast flexible films from reaction solutions. Films cast from the reaction mixtures in which pyridine was used as the acid acceptor resulted in brittle films.

In order to obtain higher molecular weight polymers, the Yamazaki² reaction was investigated as a possible route to the desired polymers. A model polymerization was run with a commercially

available diamine, 4,4'-oxydianiline, and an anhydride, trimellitic acid anhydride. The usual monomers for the Yamazaki reaction are a diamine and a dicarboxylic acid. In order to prepare the title polymers utilizing the Yamazaki reaction a diamine would have to be reacted with an anhydride carboxylic acid to yield 29 as shown below.

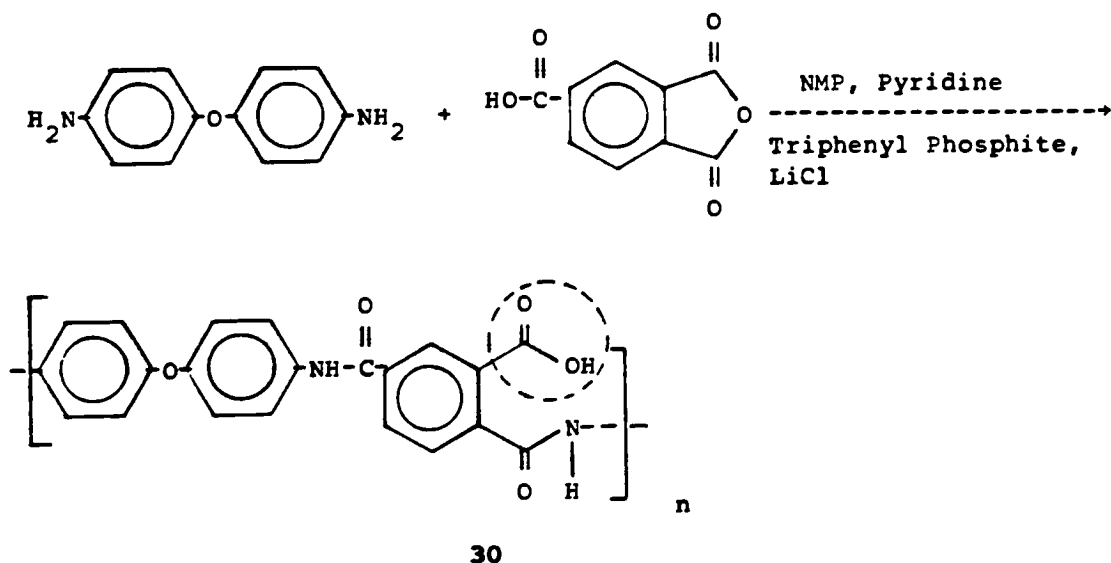


where AR = aromatic group

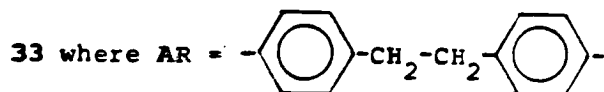
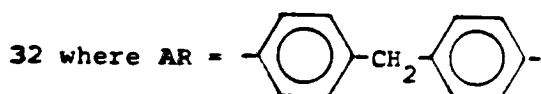
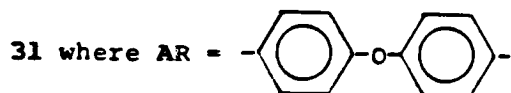
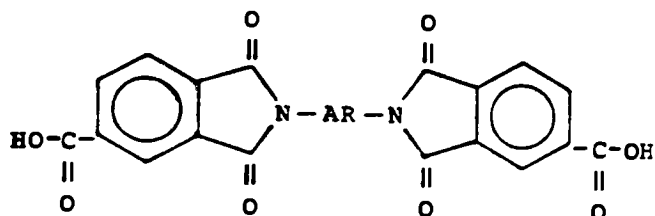
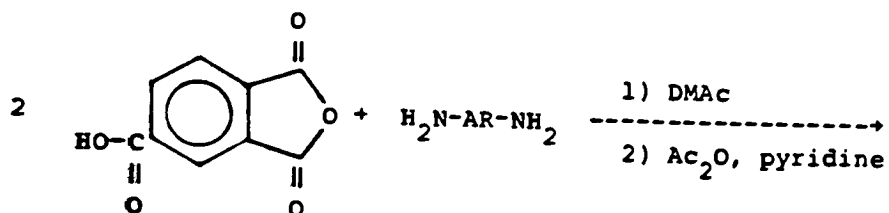
To our knowledge this type of polymerization has never been attempted.

The Yamazaki reaction utilizes an anhydrous solvent, N-methyl pyrrolidone, an acid acceptor, pyridine, triphenyl phosphite, and lithium chloride. Upon addition of 4,4'-oxydianiline and trimellitic acid anhydride to the reaction solvent and subsequent heating to 90°C

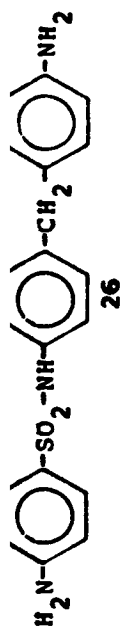
a viscous liquid formed at first, which turned into a gel-like material. Addition of absolute methanol, suction filtration, washing, and drying gave a brilliant yellow polyamic acid 30 which could not be dissolved in N,N-dimethylacetamide or concentrated sulfuric acid for viscosity measurements. Because the polyamic acid was insoluble in these solvents, it was postulated that the product from this reaction was highly crosslinked. The group circled in the reaction below represents a possible site where crosslinking and/or branching may occur.



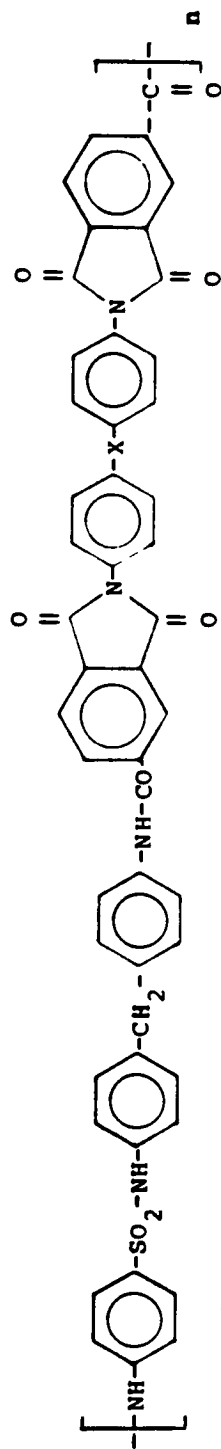
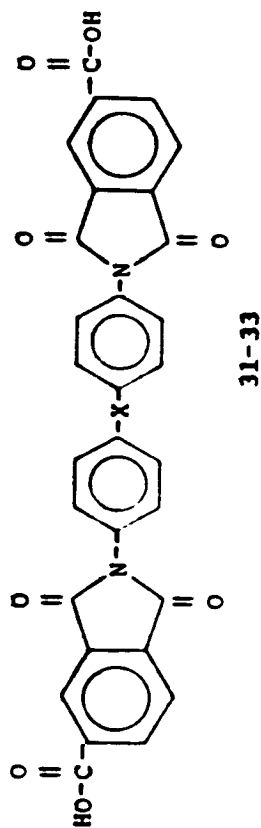
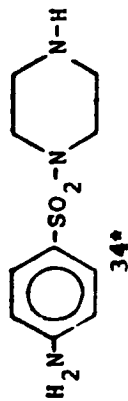
This result forced us to consider another synthetic route utilizing different monomers while still employing the Yamazaki reaction. The technique of Wrasidlo and Augl¹³ was used. The formation of the intermediate polyamic acid was avoided by synthesizing monomers 31 - 33 containing preformed imide linkages which are shown on the next page.



Using this scheme, higher molecular weight polymers, 35-40, were obtained by reacting diamine monomers 26 and 34 with dicarboxylic acids 31-33 containing preformed imide links. The general polymerization scheme is shown on the next page.



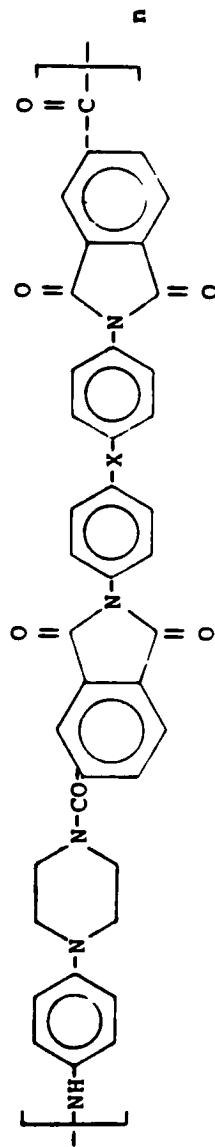
or



NMP, pyridine

LiCl, triphenyl phosphite

X = -O- (35), -CH₂-(36), -CH₂CH₂- (37)



X = -O- (38), -CH₂-(39), -CH₂CH₂- (40)

* Prepared by Thevarak Rochanapruk

Table IX: Summary of the Yamazaki Reaction Utilizing a Diamine And a Bisimide Diacid.

<u>Polymer</u>	<u>Yield(%)</u>	<u>η_{inh} (dL/gm)^a</u>	<u>Tg(°C)^c</u>	<u>PDT^{d,e}</u>	<u>% wt. loss^d at 360°C</u>	<u>Film Forming</u>	<u>Film Color</u>	<u>Film Flexibility</u>
35	97	0.54	289	361	11.28	yes	clear yellow-green	flexible
36	89	0.27	266	362	8.53	yes	clear yellow-green	semi-flexible
37	85	0.29	--	367	4.95	yes	clear yellow-green	flexible
38	97	0.54	303	393	9.08	yes	clear, light yellow-green	flexible
39	92	0.35	314	382	6.05	yes	clear colorless	flexible
40	89	0.39 ^b	324	417	4.13	yes	opaque, off-white	flexible

a) Measured in N,N-dimethylacetamide at 25°C with a concentration of 0.1250 gm/25 ml.

b) Addition of 5% lithium chloride necessary for complete polymer solution.

c) Determined in nitrogen atmosphere at a heating rate of 20°/min.

d) Determined in nitrogen atmosphere at a heating rate of 20°/min.

e) PDT = polymer decomposition temperature.

The results of these polymerization reactions are shown in Table IX.

One advantage of the Yamazaki reaction is the utilization of a dicarboxylic acid instead of a diacid chloride. The step growth polymerization process requires high monomer purity in order to form a high molecular weight material. Since the diacid chlorides are very reactive, they can react with water in the atmosphere to form a dicarboxylic acid which is not as reactive, leading to lower molecular weight polymers.

The dryness and purity of the diamine monomers, bisimide diacids and the solvents used are important criteria in the Yamazaki reaction. All of the diamines used in this research project contained preformed sulfonamide linkages. Sulfonamide linkages can strongly associate with water or solvents by hydrogen bonding; impurities such as these will lead to the formation of low molecular weight polymers.

Polymers 35 and 38, which contained oxygen in the backbone, were obtained with the highest inherent viscosity, i.e., 0.54 dL/gm. As also would be expected polymers 37 and 40 had slightly greater inherent viscosities than polymers 36 and 39, 0.29, 0.39 dL/gm and 0.27, 0.35 dL/gm, respectively. The inclusion of an ethylene unit, rather than a methylene unit, into the polymer backbone results in a polymer having slightly better solubility properties. The longer a polymer stays in solution without precipitating, the greater the probability that a polymer with a slightly higher viscosity will be obtained.

All the prepared polymers formed films despite the low inherent

viscosities observed. The films ranged in color from green-yellow to colorless, and all films could be bent many times without breaking. Polymer 40 formed an opaque, off-white film which was flexible. Approximately five percent lithium chloride was added to get polymer 36 into solution. Leaching the film in water to remove lithium chloride did not affect the opaque nature of the film.


Glass transition temperature (T_g) is the temperature at which a polymer changes from a hard, brittle material to a rubber-like material. The glass transition temperature is a measure of the ease of torsion of the backbone bonds. Glass transition temperatures of the prepared polymers were determined by differential scanning calorimetry and ranged from 266 to 324°C.

Polymers 38 to 40, containing the piperazine unit in the backbone, showed the highest glass transition temperatures. Glass transition temperatures of 303, 314, and 324°C were observed for polymers 38, 39, and 40, respectively. This was due to the presence of the piperazine unit in polymers 38 to 40 which is a shorter and more rigid diamine monomer unit than that found in polymers 35 to 37. The rigidity of the piperazine unit allowed polymers 38 to 40 to undergo a high degree of ordering, thus increasing the glass transition temperatures of this polymer series.

Of special interest were those glass transition temperatures obtained for polymers 36 and 37, whose backbone contained the 4,4'-methylenedianiline unit. On heating polymer 36 in the differential scanning calorimeter for the first time a thermogram was obtained which showed a series of possible degradation reactions.

Polymer 37 did not have a recognizable glass transition temperature, even after several heatings. This phenomena may be explained by the glass transition temperature occurring at or near the decomposition temperature of polymer 37, thereby masking the glass transition temperature.

The thermal stability of the prepared copoly(amide-imide-sulfonamides) was measured by thermogravimetric analysis at a heating rate of twenty degrees per minute in nitrogen. Thermal stability can be defined as that temperature where severe weight loss of the polymer occurs. All prepared copoly(amide-imide-sulfonamides) showed approximately a two to eight percent weight loss at low temperatures which was attributed to the loss of entrapped solvents and water.

The lower thermal stability of the sulfonamide linkage resulted in polymer decomposition temperatures ranging from 361 to 417°C in nitrogen. Polymers 38, 39, and 40, containing the piperazine unit in the backbone, also had the highest thermal stabilities, 393, 382, and 417°C, respectively. This can be explained by the cyclic nature of the sulfonamide linkage, i.e., , rather than the aliphatic nature of the sulfonamide linkage, i.e., $\text{-NH-SO}_2\text{-}$, which polymers 25 and 37 possess.

Thermogravimetric analysis was also performed on polymers 35, 38, 39, and 40 in an air atmosphere. No significant change in polymer decomposition temperature was obtained for polymer 35, which contained the 4,4'-methylenedianiline unit in the backbone. Thus, it was shown that thermooxidative and thermal bond degradation occurred at approximately the same temperature in polymer 35.

Thermogravimetric analysis conducted in an air atmosphere for polymer 38 showed that thermooxidative degradation occurred 26°C lower than thermal degradation. Also, for polymers 39 and 40, thermooxidative degradation occurred 22° and 65°C lower, respectively, than thermal degradation.

5.0 EXPERIMENTAL

5.1 General Information

1) N,N-dimethylacetamide and N-methyl-2-pyrrolidone were distilled under reduced pressure and stored under nitrogen. Pyridine was fractionally distilled from a flask containing sodium hydroxide pellets and was stored over fresh sodium hydroxide pellets, under a nitrogen atmosphere. Propylene oxide was fractionally distilled at atmospheric pressure and stored under nitrogen.

2) All melting points were determined in capillaries using a Mel-temp apparatus and are uncorrected.

3) ^1H NMR spectra were determined using a Hitachi Perkin-Elmer R-20 operating at 60 MHz with tetramethylsilane as the internal standard.

4) Unless otherwise stated, infrared spectra of all samples were done as potassium bromide pellets or films using a Perkin-Elmer PE-681 infrared spectrophotometer and can be found in the appendix.

5) Dry column chromatography was done using Kieselgel 60 F254 as the stationary phase.

6) All concentration processes were done by using a Buchi rotary evaporator with the water bath temperature not exceeding 60°C.

7) Trimellitic anhydride acid chloride, 4,4'-oxydianiline, 4,4'-methylenedianiline, N-acetamidobenzenesulfonyl chloride, lithium chloride, and N-methyl-2-pyrrolidone were obtained from Aldrich Chemical Co.; triphenyl phosphite and triethyl amine were obtained from Eastman-Kodak Co.; pyridine and propylene oxide were obtained from J. T. Baker Chemical Co.

8) Thermal gravimetric analyses of all polymers were determined by using a Perkin-Elmer TGS-2 thermal analysis under nitrogen atmosphere with a heating rate of 20.0°C per minute and can be found in the appendix.

9) Differential Scanning Calorimetry analyses were determined using a Perkin-Elmer DSC-4 with a heating range of 20°C per minute and a range of 0.5-2.0 mcal per second and two examples can be found in the appendix. In all cases the midpoint of the endotherm of the third run was taken as the Tg.

10) Thin layer chromatographic analyses were carried out on Eastman Chromatogram sheets (13181 silica gel).

11) Inherent viscosities were determined using a Canon viscometer no. 1 C426 at a constant temperature of 25°C with a polymer concentration of 0.1250 grams in 25 ml of N,N-dimethylacetamide.

5.2 Synthesis of N-acetylimino-1,4-phenylenesulfonylimino-1,4-phenylenemethylene-1,4-phenyleneamine 20

In a 4000 ml Erlenmeyer flask equipped with a thermometer and magnetic stirrer/hot plate, 90.0 gm (0.45 mole) of 4,4'-methylene-dianiline was dissolved in 1700 ml of distilled tetrahydrofuran. The solution was magnetically stirred until all the 4,4'-methylene-dianiline was dissolved. This solution then had added to it 30.7 ml (0.22 mole) of triethyl amine and the temperature of the reaction medium was then brought to 58-61°C. To this heated solution was added dropwise from a 1000 ml separatory funnel over a 2½ hour period 53.06 gm (0.22 mole) of N-acetamidobenzenesulfonyl chloride in 2000 ml of distilled tetrahydrofuran. After the addition was completed, the solution was left to stir overnight without heating. The precipitate which formed was suction filtered from solution and evaporation of this filtrate gave a dark brown viscous syrup. This syrup was chromatographed using hexanes/ethyl acetate/acetone (3:2:1) as the mobile phase and silica gel as the stationary phase. A tan crystalline product 20 was obtained with an $R_f = 0.41$ (ethyl acetate/hexanes/acetone (2:1:1)). The product was dried overnight in a vacuum oven at 70°C and was used as such for further transformation.

yield = 48.87 gm (56%)

m.p. 171-181°C

IR data (KBr): $\nu = 3340 \text{ cm}^{-1}$ (N-H), $\nu = 1680 \text{ cm}^{-1}$ (C = O),

$\nu = 1150 \text{ cm}^{-1}$ (S = O)

Synthesis of N-acetylimino-1,4-phenylenesulfonylimino-1,4-phenylene-oxy-1,4-phenyleneamine 21

Using the procedure previously described in the synthesis of 20, 112.74 gm (0.563 mole) of 4,4'-oxydianiline and 38.6 ml (0.277 mole) of triethyl amine in 1500 ml of distilled tetrahydrofuran was reacted with 64.73 gm (0.277 mole) of N-acetamidobenzenesulfonyl chloride in 1900 ml of distilled tetrahydrofuran. The product was dried overnight in a vacuum oven at 70°C and was used as such for further transformation.

yield = 69.75 gm (63%)

m.p. 202.5-208°C

IR data (KBr): $\nu = 3220 \text{ cm}^{-1}$ (N-H), $\nu = 1675 \text{ cm}^{-1}$ (C = O),

$\nu = 1150 \text{ cm}^{-1}$ (S = O)

5.3 Synthesis of Amino-1,4-phenylenesulfonylimino-1,4-phenylene-methylene-1,4-phenyleneamine 26

Using a 300 ml one neck round bottom flask fitted with a condenser and a magnetic stirrer, 10 gm (0.025 mole) of 20 was treated with 125 ml of 6M hydrochloric acid. The mixture was refluxed for 25 minutes. The mixture was then cooled in an ice water bath and was neutralized by the careful additions of a saturated solution of sodium bicarbonate to give a light yellow-brown precipitate of 26, which was suction filtered and dried overnight in a vacuum oven at 70°C.

yield 6.90 gm (77%)

This crude product was dissolved in a 1:1 mixture of absolute ethanol and acetone and was chromatographed using hexanes/ethyl acetate/acetone (3:2:1) as the eluting solvent with silica gel as the stationary phase. This gave cream colored crystals of 26. The product was further purified by recrystallization from absolute methanol. The recrystallized product was dried one day in a vacuum oven at 70°C. It was further dried in a pistol over phosphorus pentoxide and refluxing cyclohexane for two days.

$$R_f = 0.65$$

$$\text{m.p. (}^{\circ}\text{C)} \text{ } 174\text{-}175$$

$$\text{IR data (KBr): } \nu = 3280 \text{ cm}^{-1} \text{ (N-H), } \nu = 1145 \text{ cm}^{-1} \text{ (S = O)}$$

This product was then used as such for the polymerization process.

Synthesis of Amino-1,4-phenylenesulfonylimino-1,4-phenyleneoxy-1,4-phenyleneamine 27

Using the same procedure previously described, 15 gm (0.038 mole) of 21 was treated with 150 ml of 6M hydrochloric acid for 30 minutes. The cooled reaction mixture was neutralized with a saturated sodium bicarbonate solution to give the crude solid diamine product 27 which was tan in color and was dried overnight in a vacuum oven at 70°C.

yield = 8.75 gm (65%)

This crude product was dissolved in a 1:1 mixture of absolute ethanol and acetone and was chromatographed using hexanes/ethyl acetate/acetone (3:2:1) as the eluting solvent with silica gel as the stationary phase. This gave a dark brown viscous syrup, which upon covering with hexanes and allowing to stand overnight at a temperature of -25°C, gave a cream colored crystalline material. This product was further purified by recrystallization from isopropanol and was dried in the same manner as 26.

$R_f = 0.66$

m.p. 143.5-144°C

IR data (KBr): $\nu = 3320 \text{ cm}^{-1}$ (N-H), $\nu = 1150 \text{ cm}^{-1}$ (S = O)

This product was then used as such for the polymerization process.

5.4 General Low Temperature Solution Polymerization Procedure

Using a 50 ml one neck round bottom flask, the diamine was dissolved in 10 ml of distilled N,N-dimethylacetamide containing 5 ml of propylene oxide. The solution was stirred and chilled in an ice bath for 30 minutes. The acid chloride was added rapidly to the stirring mixture. The mixture was left stirring at 0-3°C for six hours and overnight at 21-23°C.

The polymer was obtained by pouring the mixture into a beaker containing 200 ml of cold distilled water. The polymer was suction filtered and dried in a vacuum oven at 90°C for one day.

5.5 General Yamazaki Polymerization Procedure

To a 25 ml two necked pear shaped flask fitted with condenser, a nitrogen inlet valve, and equipped with a magnetic stir bar, was added 1.41×10^{-3} mole of the diamine, 1.41×10^{-3} mole of the bisimide diacid, 0.1402 gm (4 wt %) lithium chloride, 2.75 ml N-methyl-2-pyrrolidone, 0.70 ml pyridine, and 0.74 ml triphenyl phosphite. An oil bath and hot plate/magnetic stirrer was used to bring the temperature of the reaction medium to 95-100°C. The solution was stirred vigorously for 12 hours under nitrogen. When cooled the polymer was precipitated from solution by the addition of 200 ml of absolute methanol. The precipitated polymer was collected by suction filtration and dried in a vacuum oven at 90°C for one day.

Synthesis of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylenemethylene-1,4-phenyleneimino-1,3-phenylenecarbonyl carboxylic acid) amic acid 28

Using the low temperature solution polymerization procedure, 0.9967 gm (2.82×10^{-3} mole) of 26 was reacted with 0.5938 gm (2.82×10^{-3} mole) of trimellitic anhydride acid to produce polymer 28.

yield 1.5402 gm (>100%)

$\eta_{inh} = 0.08$ dL/gm

Synthesis of poly(imino-1,4-phenyleneoxyimino-1,3-phenylenecarbonyl
carboxylic acid) amic acid 30

Using the general Yamazaki polymerization procedure, 1.0012 gm (0.005 mole) of 4,4'-oxydianiline was reacted with 0.9606 gm (0.005 mole) of trimellitic acid anhydride in 10.0 ml N-methyl-2-pyrrolidone, 7.5 ml pyridine, 2.62 ml triphenyl phosphite containing 0.7066 gm of lithium chloride to give polymer 30.

Synthesis of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylenemethylene-1,4-phenyleneimino)-oxy-bis[N-(4-phenylene)-4'-(carbonyl)phthalimide 35.

Using the general Yamazaki polymerization procedure, 0.4984 gm (1.41×10^{-3} mole) of 26 was reacted with 0.7733 gm (1.41×10^{-3} mole) of 31 in 2.75 ml N-methyl-2-pyrrolidone, 0.70 ml pyridine, 0.74 ml triphenyl phosphite containing 0.1402 gm of lithium chloride to give polymer 35.

yield = 1.3236 (97%)

η_{inh} = 0.54 dL/gm

T_g = 289°C

PDT = 361°C

IR data (film): ν = 3280 cm^{-1} (N-H),

ν = 1725 cm^{-1} (C = O),

ν = 1156 cm^{-1} (S = O)

Synthesis of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylene-methylene-1,4-phenyleneimino)-methylene-bis[N-(4-phenylene)-4'-(carbonyl)phthalimide 36

Using the general Yamazaki polymerization procedure, 0.4984 gm (1.41×10^{-3} mole) of 26 was reacted with 0.7706 gm (1.41×10^{-3} mole) of 32 in 2.75 ml N-methyl-2-pyrrolidone, 0.70 ml pyridine, 0.74 ml triphenyl phosphite containing 0.1402 gm of lithium chloride to give polymer 36.

yield = 1.2080 gm (89%)

$\eta_{inh} = 0.27$ dL/gm

Tg = 266°C

IR data (film): $\nu = 3275 \text{ cm}^{-1}$ (N-H),

$\nu = 1725 \text{ cm}^{-1}$ (C = O),

$\nu = 1156 \text{ cm}^{-1}$ (S = O)

Synthesis of poly(imino-1,4-phenylenesulfonylimino-1,4-phenylene-methylene-1,4-phenylimino)-ethylene-bis[N-(4-phenylene)-4'-(carbonyl)phthalimide 37

Using the general Yamazaki polymerization procedure, 0.4984 gm (1.41×10^{-3} mole) of 26 was reacted with 0.7903 gm (1.41×10^{-3} mole) of 33 in 2.75 ml N-methyl-2-pyrrolidone, 0.70 ml pyridine, 0.74 ml triphenyl phosphite containing 0.2103 gm of lithium chloride to give polymer 37.

yield = 1.2283 gm (85%)

η_{inh} = 0.29 dL/gm

Tg = none observed

PDT = 367°C

IR data (film): ν = 3300 cm^{-1} (N-H),

ν = 1720 cm^{-1} (C = O),

ν = 1155 cm^{-1} (S = O)

Synthesis of poly(imino-1,4-phenylenesulfonylpiperazinylene)-oxy-bis[N-(4-phenylene)-4'-(carbonyl)phthalimide 38

Using the general Yamazaki polymerization procedure, 0.3403 gm (1.41×10^{-3} mole) of 34 was reacted with 0.7733 gm (1.41×10^{-3} mole) of 31 in 2.75 ml N-methyl-2-pyrrolidone, 0.70 ml pyridine, 0.74 ml triphenyl phosphite containing 0.1402 gm of lithium chloride to give polymer 38.

yield = 1.1727 gm (97%)

$\eta_{inh} = 0.54$ dL/gm

Tg = 303°C

PDT = 393°C

IR data (film): $\nu = 3282$ cm⁻¹ (N-H),

$\nu = 1725$ cm⁻¹ (C = O),

$\nu = 1160$ cm⁻¹ (S = O)

Synthesis of poly(imino-1,4-phenylenesulfonylpiperazinylene)-
methylen-bis[N-(4-phenylene)-4'-(carbonyl)phthalimide 39

Using the general Yamazaki polymerization procedure, 0.3403 gm (1.41×10^{-3} mole) of 34 was reacted with 0.7706 gm (1.41×10^{-3} mole) of 32 in 2.75 ml N-methyl-2-pyrrolidone, 0.70 ml pyridine, 0.74 triphenyl phosphite containing 0.1402 gm of lithium chloride to give polymer 39.

yield = 1.1010 gm (92%)

η_{inh} = 0.35 dL/gm

T_g = 314°C

PDT = 382°C

IR data (film): ν = 3280 cm^{-1} (N-H),

ν = 1720 cm^{-1} (C = O),

ν = 1160 cm^{-1} (S = O)

Synthesis of poly(imino-1,4-phenylenesulfonylpiperazinylene)-ethylene-bis[N-(4-phenylene)-4'-(carbonyl)phthalimide 40

Using the general Yamazaki polymerization procedure, 0.3403 gm (1.41×10^{-3} mole) of 34 was reacted with 0.7903 gm (1.41×10^{-3} mole) of 33 in 2.75 ml N-methyl-2-pyrrolidone, 0.70 ml pyridine, 0.74 triphenyl phosphite containing 0.1402 gm of lithium chloride to give polymer 40.

yield = 1.0872 gm (89%)

η_{inh} = 0.39 dL/gm

Tg = 324°C

PDT = 417°C

IR data (film): ν = 3100 cm^{-1} (N-H),

ν = 1725 cm^{-1} (C = O),

ν = 1155 cm^{-1} (S = O)

4.0 Conclusion

Six novel copoly(amide-imide-sulfonamides) have been synthesized and characterized. The copoly(amide-imide-sulfonamides) 35 and 38, containing oxygen in the backbone, were shown to have the best viscosities. The copoly(amide-imide-sulfonamides) 37 and 40 containing an ethylene unit in the backbone, were shown to have the best thermal properties. These materials are potential membrane candidates for reverse osmosis and should be investigated further. Of special interest should be the preparation of polymers using the 4,4'-oxydianiline derived diamine monomer and the bisimide diacids mentioned in this research project, especially that of the bisimide diacid derived from 4,4'-oxydianiline.

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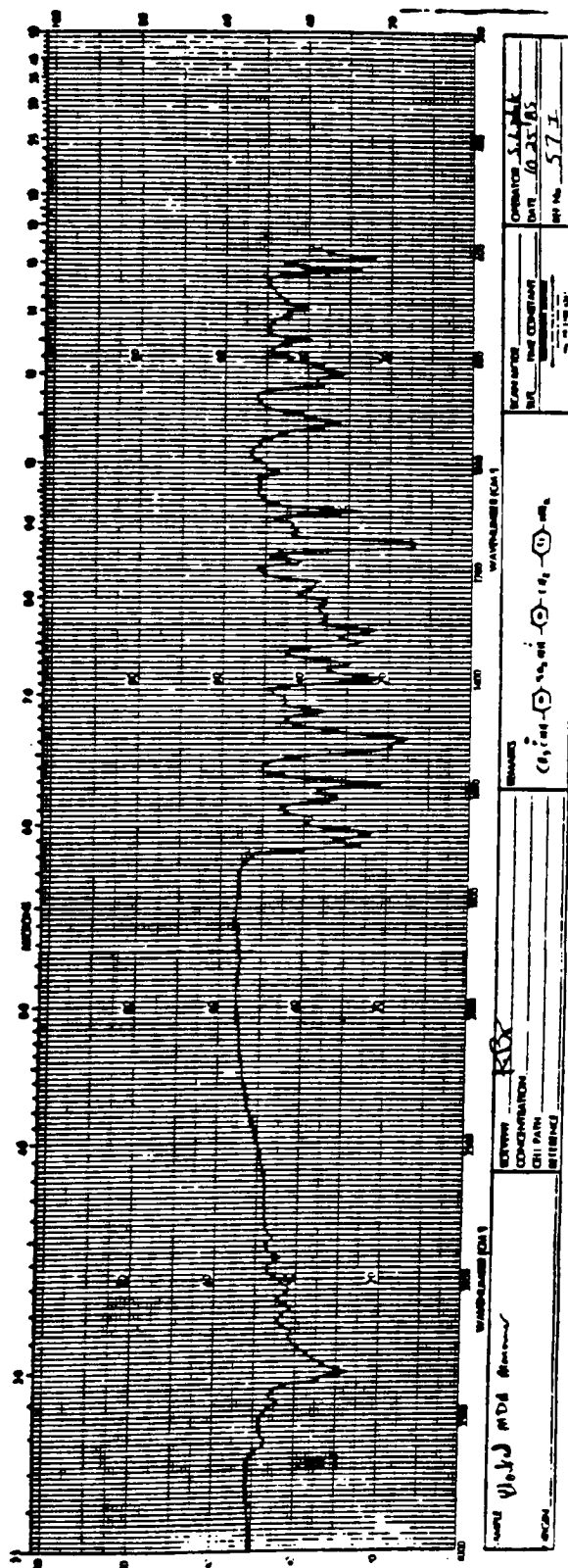


Fig. 2 IR Spectrum of amino-sulfonamido-acetanilide 20

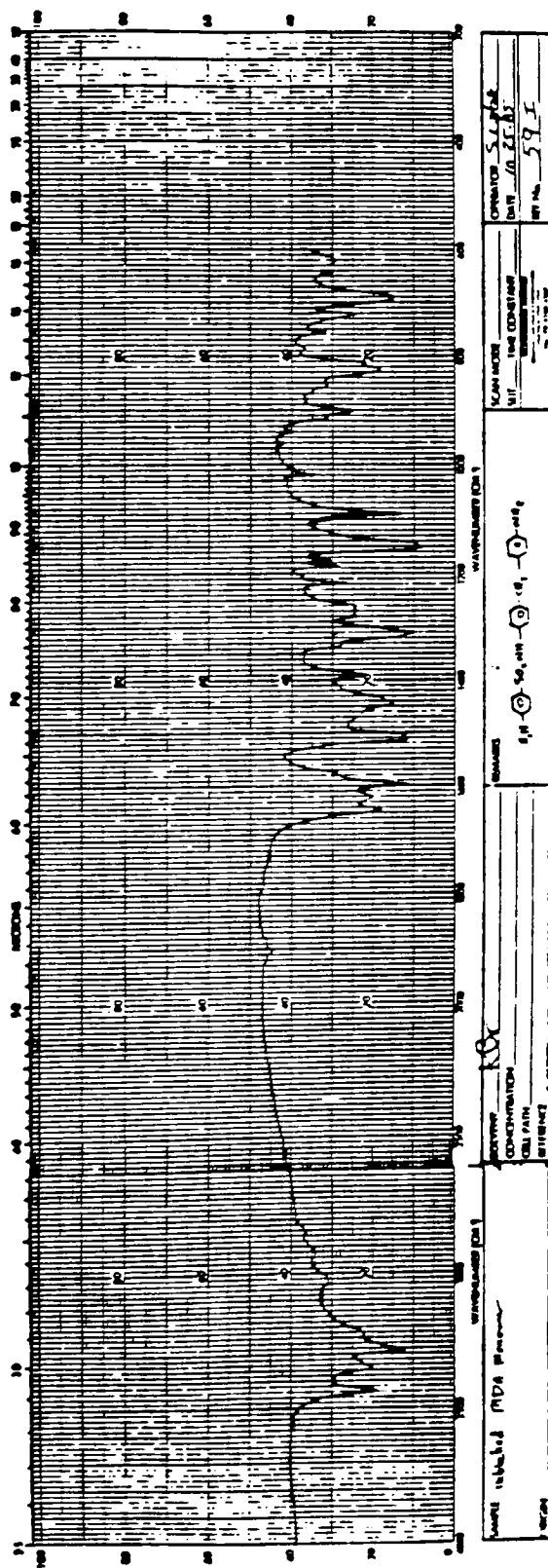


Fig. 4 IR Spectrum of diamino-sulfonamido-monomer 26

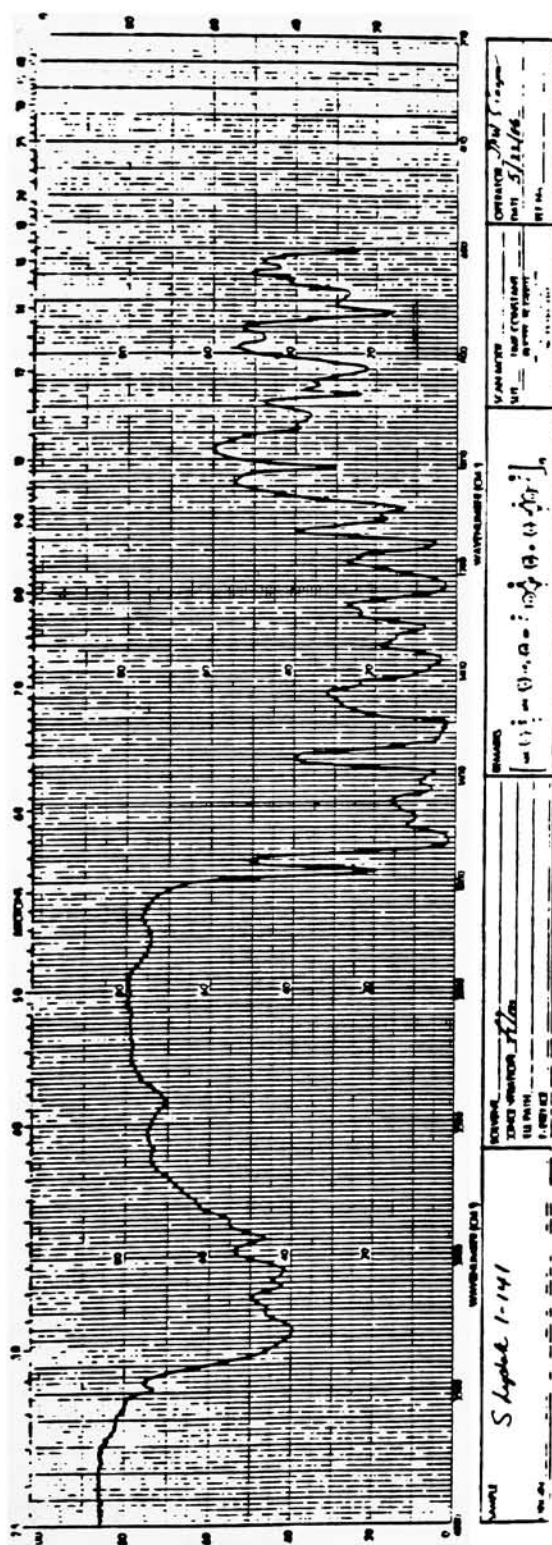


Fig. 6 IR Spectrum of polymer 35

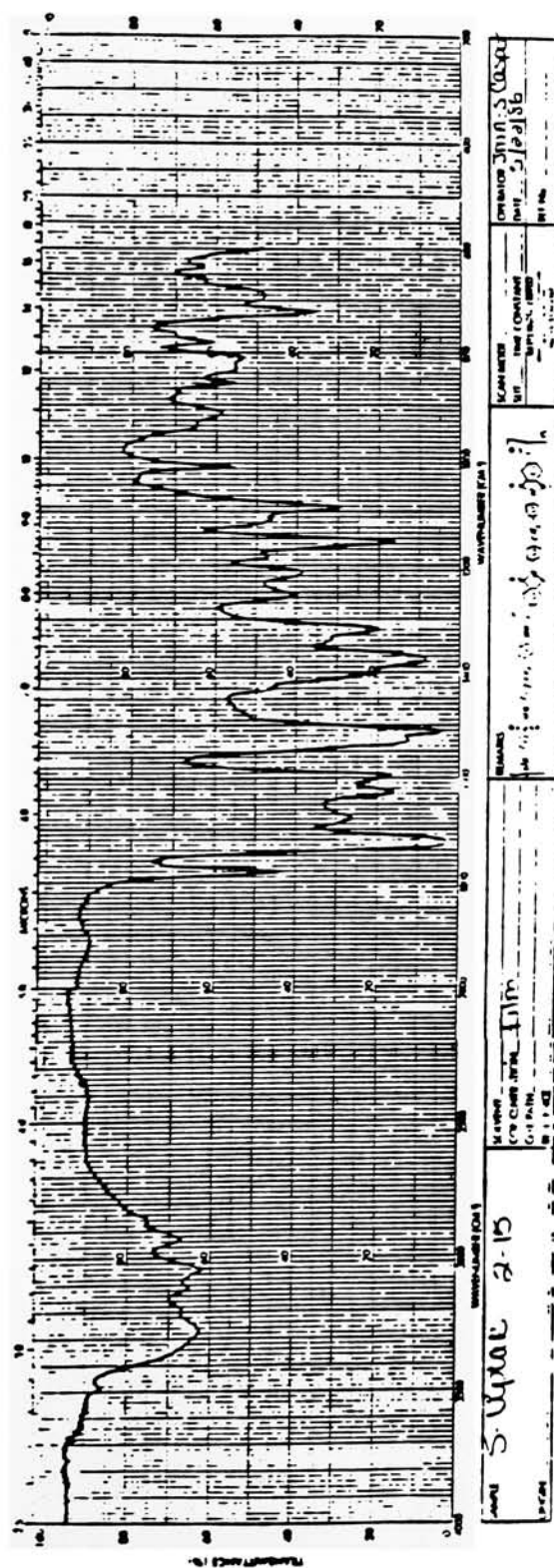


Fig. 7 IR Spectrum of polymer 36

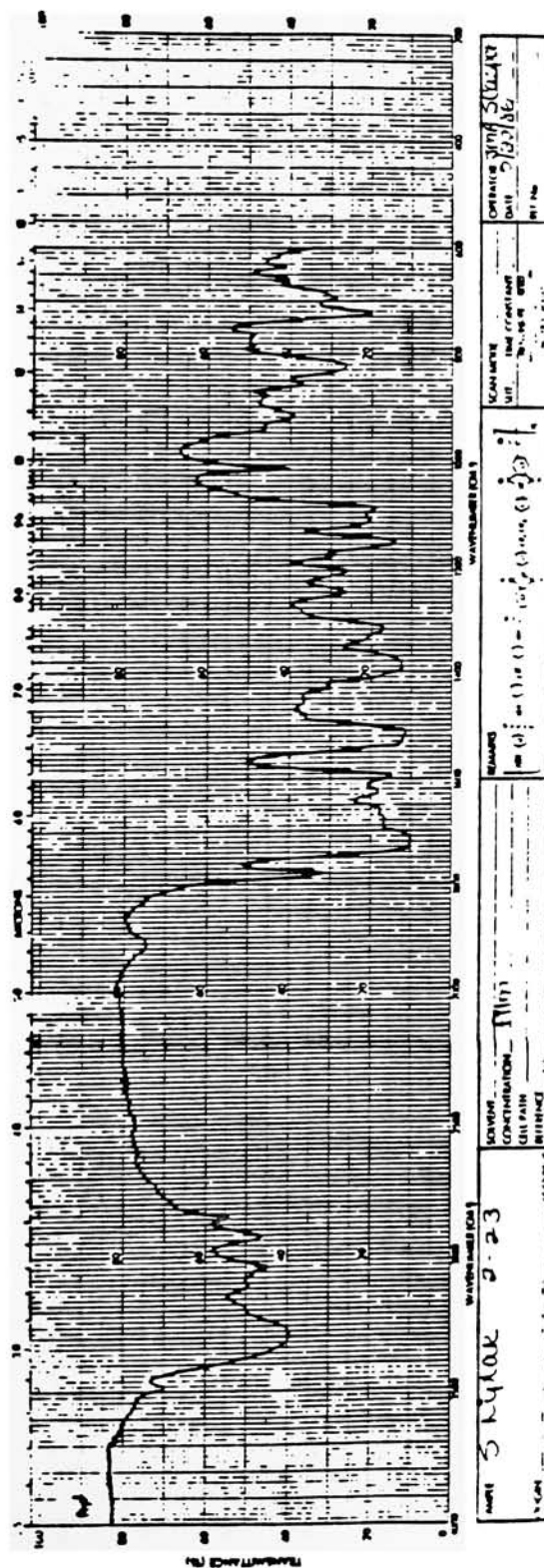


Fig. 8 IR Spectrum of polymer 37

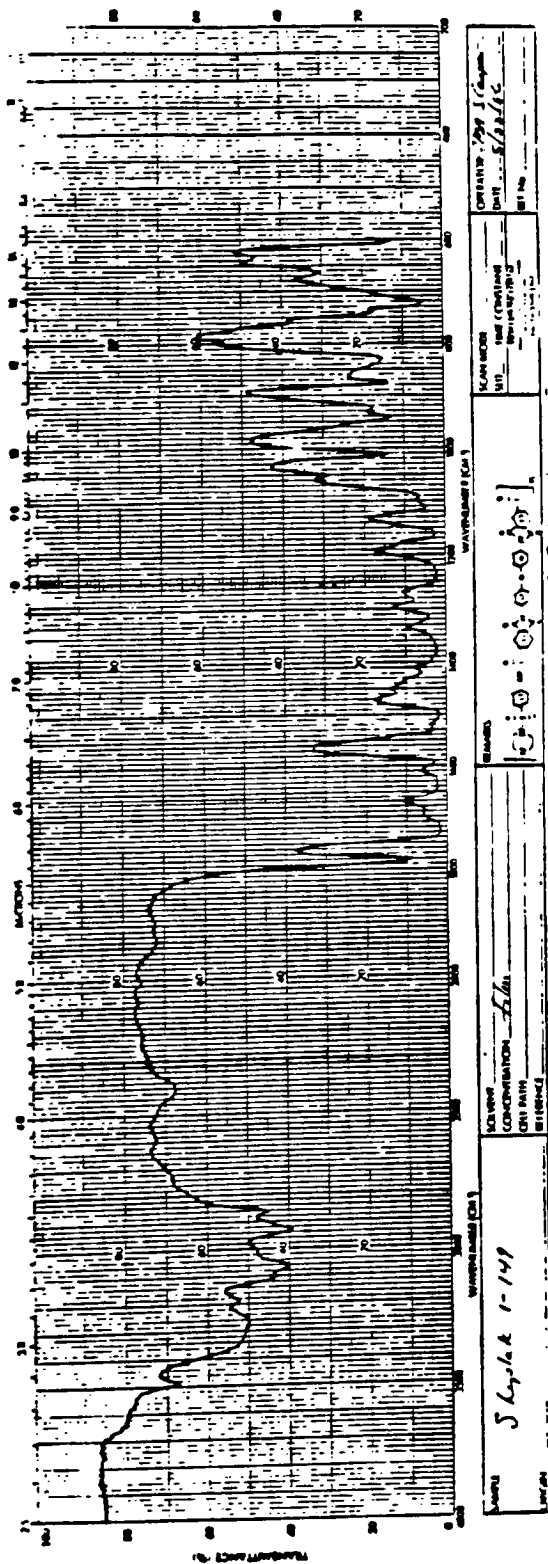


Fig. 9 IR Spectrum of polymer 38

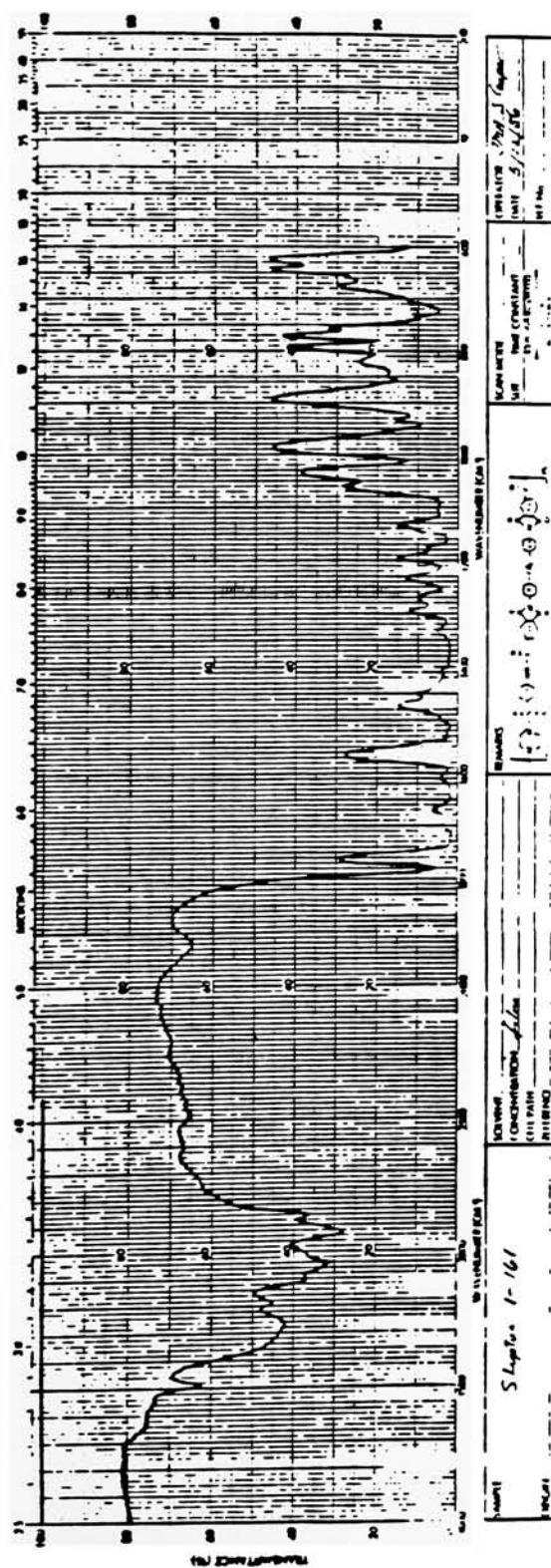


Fig. 10 IR Spectrum of polymer 39

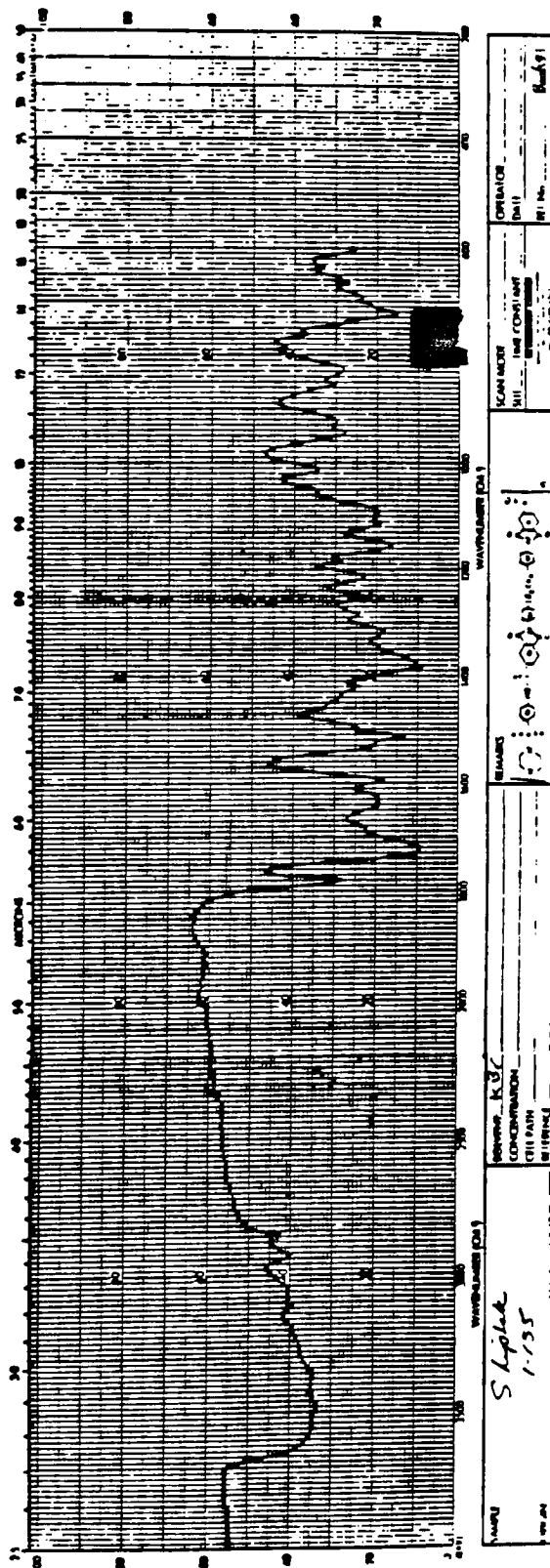


Fig. 11 IR Spectrum of polymer 40

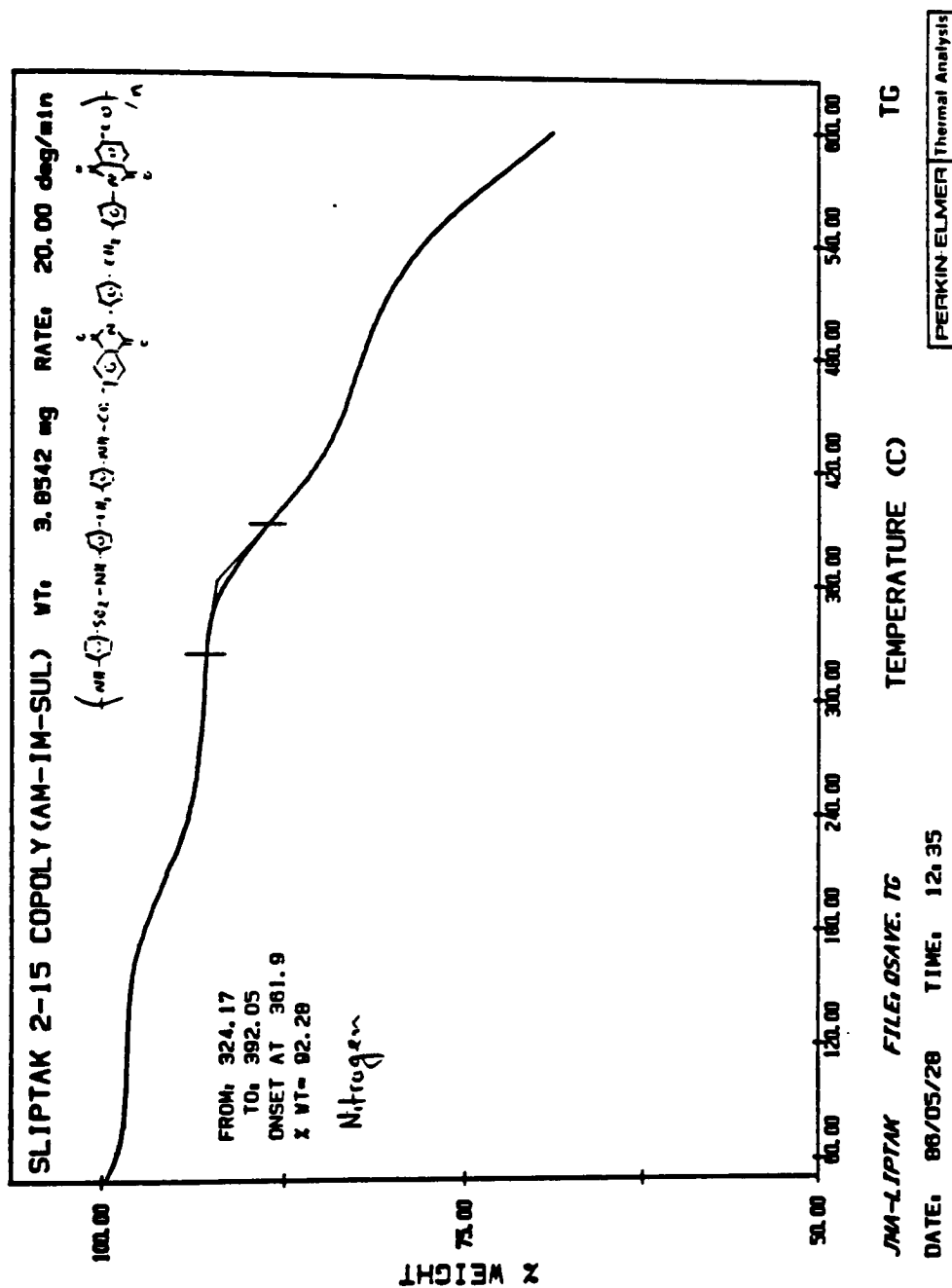


Fig. 13 TGA Curve of polymer 36 in nitrogen

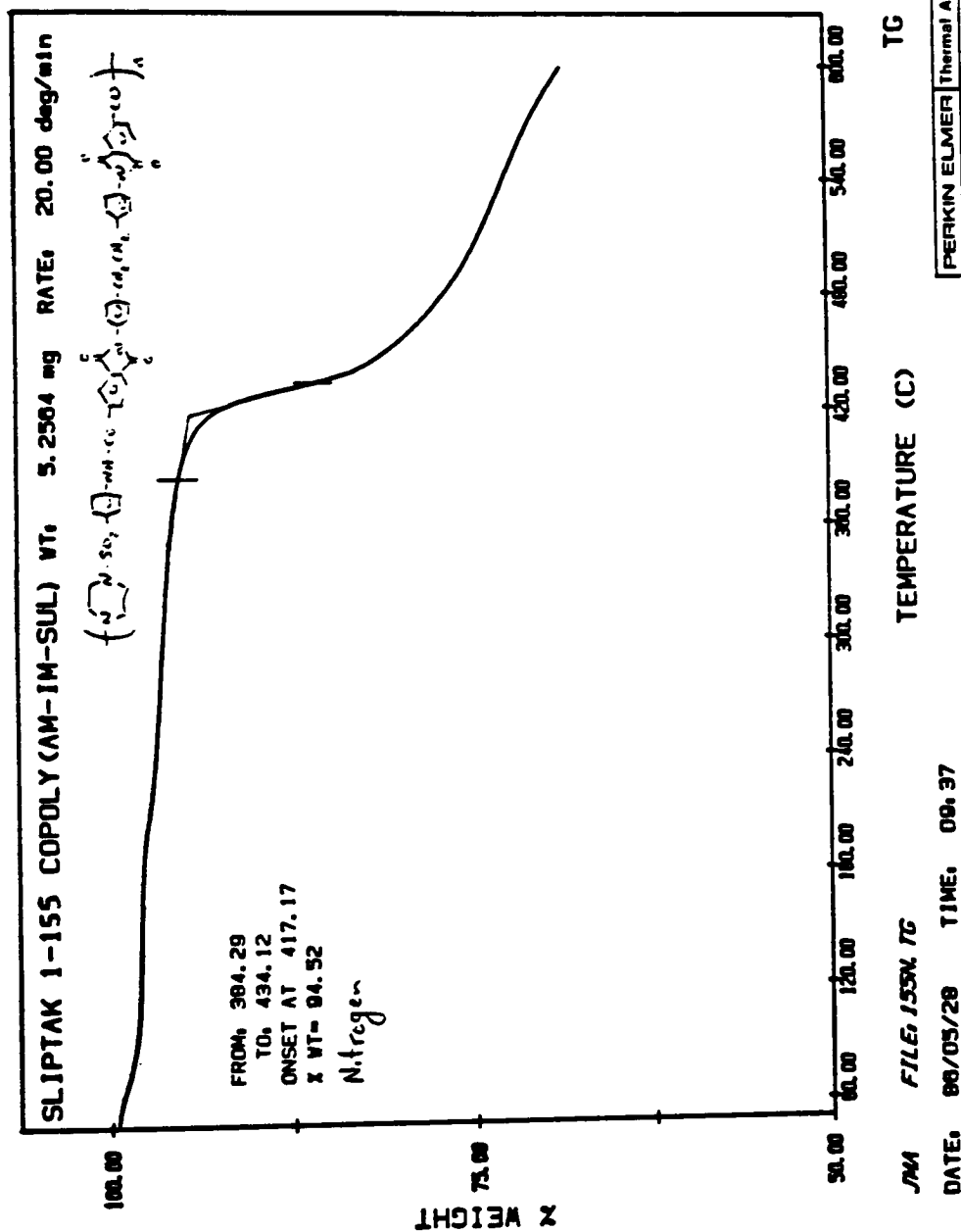


Fig. 17 TGA curve of polymer 40 in nitrogen

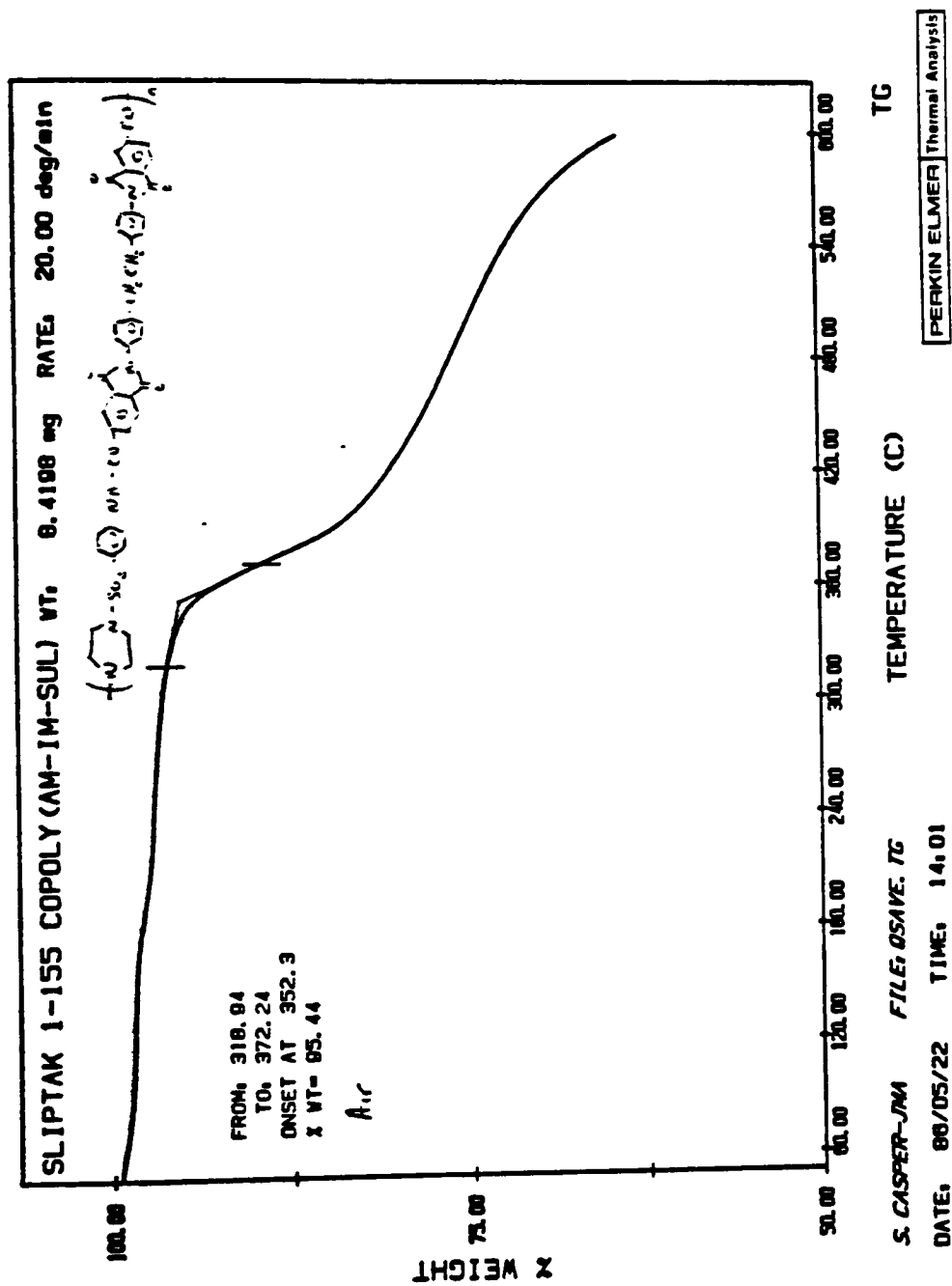
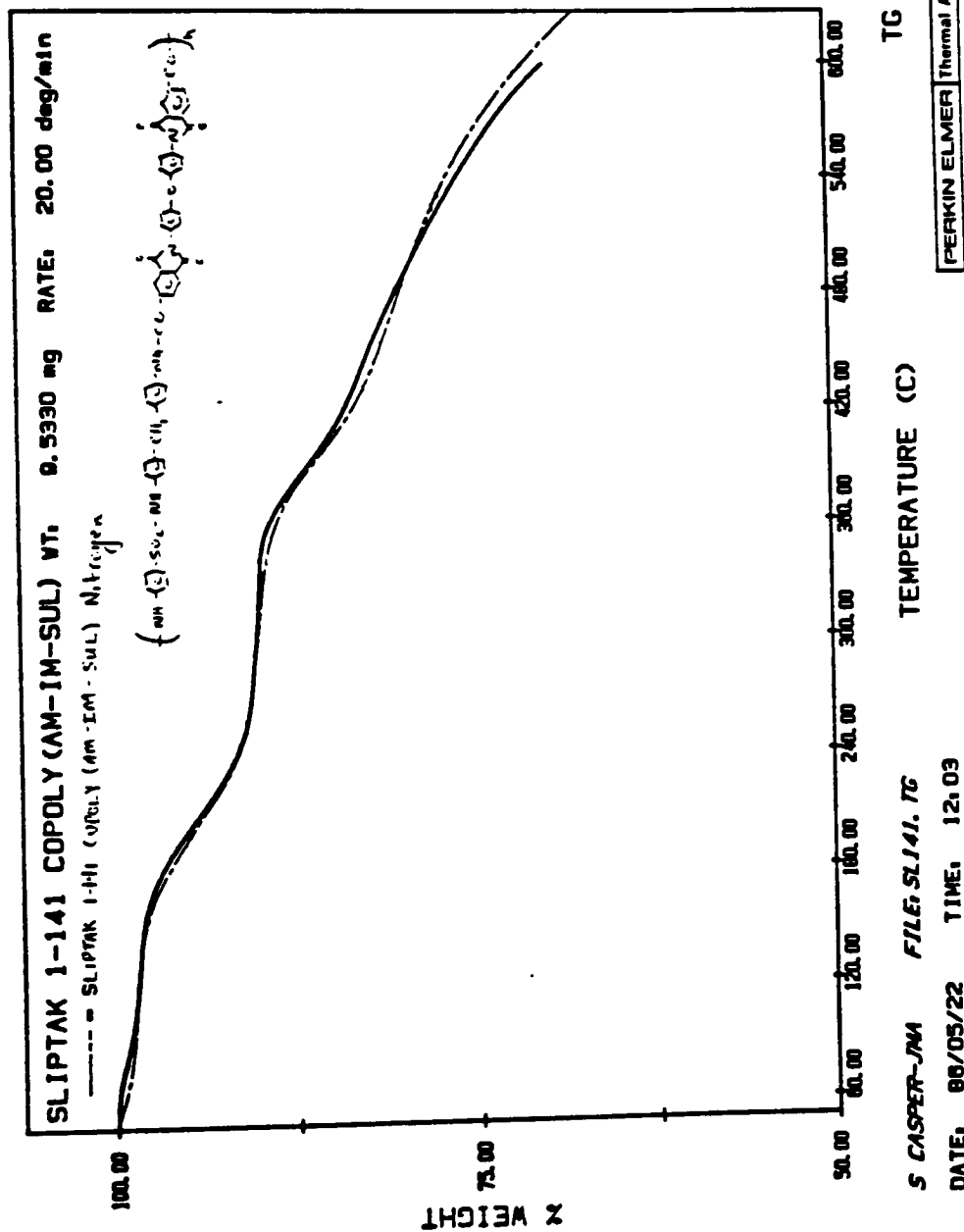


Fig. 21 TGA curve of polymer 40 in air



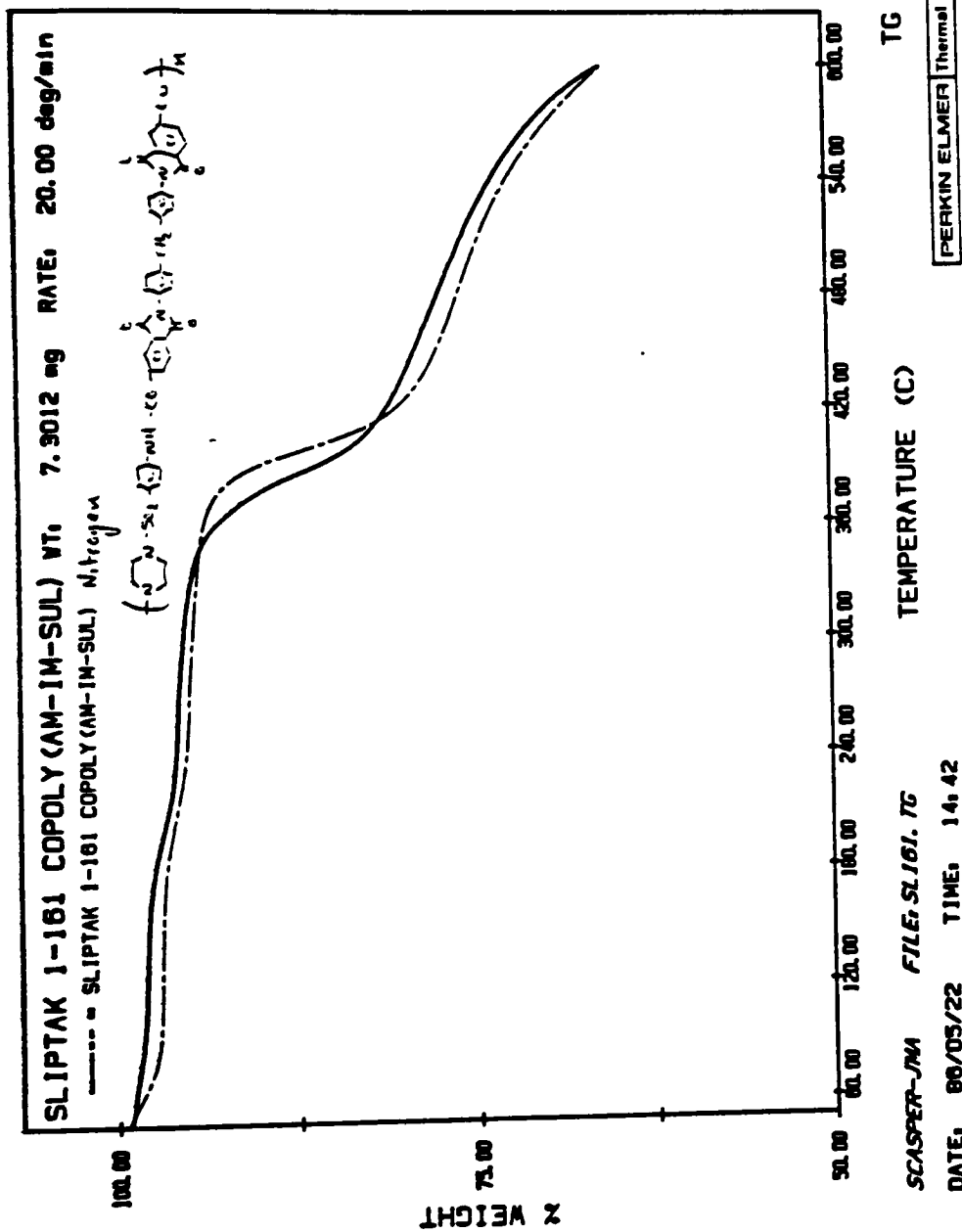


Fig. 24 TGA curve of polymer 39 (air vs. nitrogen)

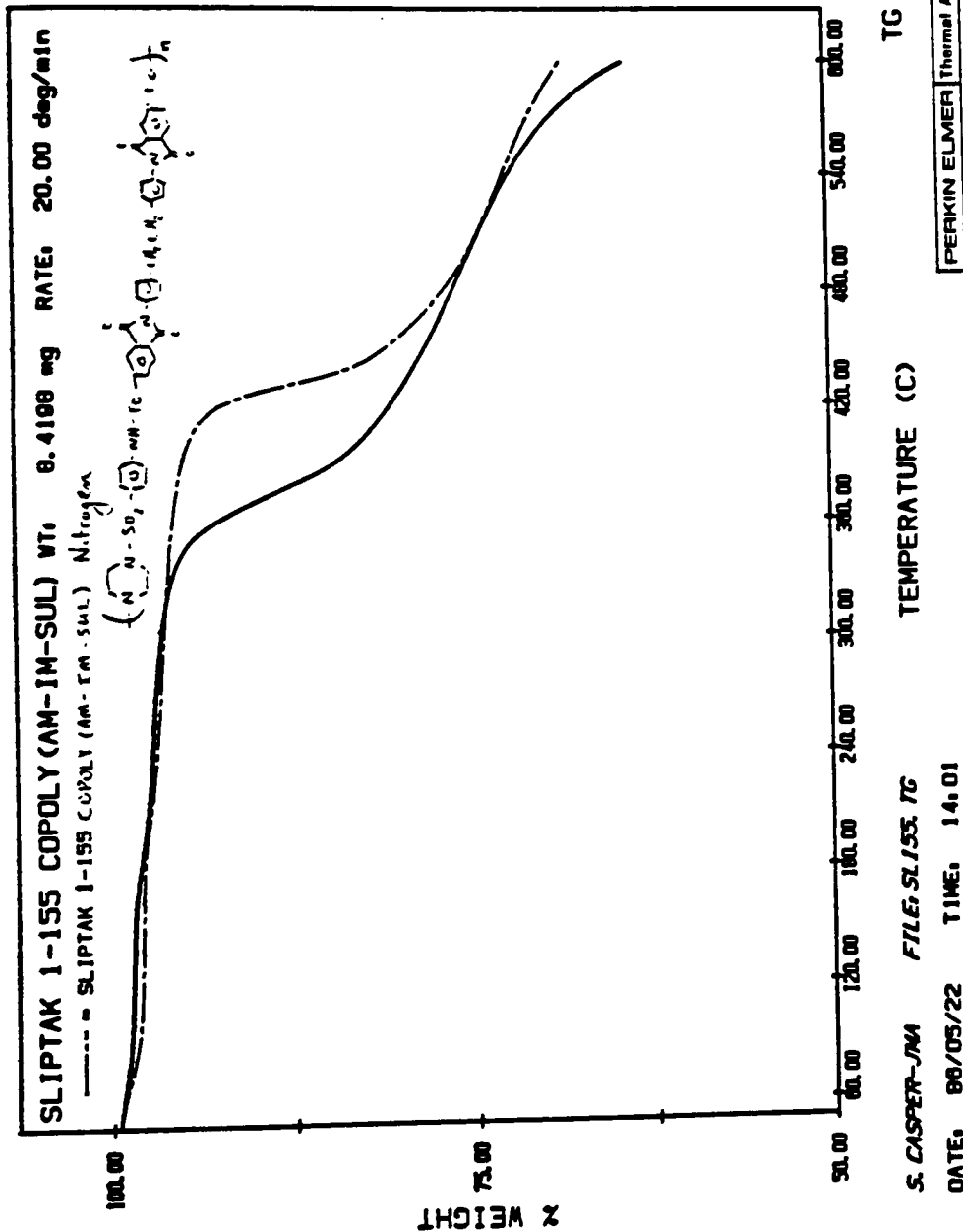


Fig. 25 TGA curve of polymer 40 (air vs. nitrogen)

